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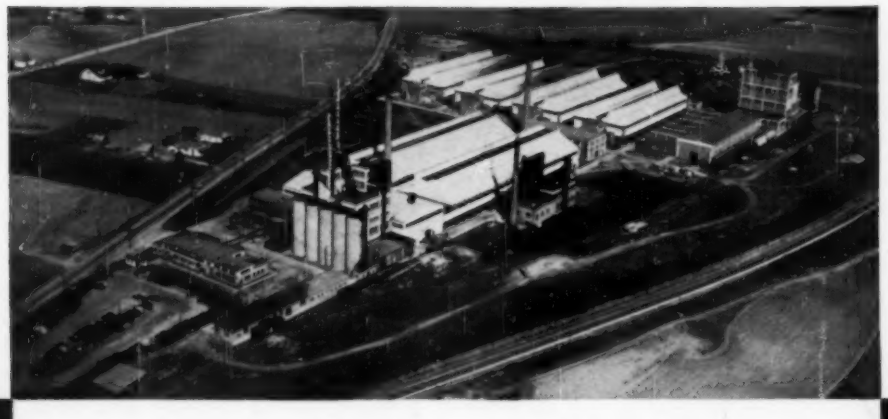

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Removal of Embrittling Gases from Zirconium[1]

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AND

D. M. Wroughton

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ABSTRACT

A process is described for the removal of dissolved oxygen from zirconium by heating the solid metal in molten or gaseous calcium. The equilibrium oxygen-zirconium ratios have been determined as a function of the time and temperature of treating. Nitrogen is not removed in the treating cycle, and contamination of the treated metal with this impurity may occur. This may be prevented by a careful control of treating temperatures. At high treating temperatures the process may be used for the removal of nitrogen from calcium.

Introduction

The embrittlement of zirconium, titanium, and vanadium metal by the interstitial solution of oxygen and nitrogen has been firmly established. Considerable progress has been made in studies concerned with the solution of these gases in metals, particularly zirconium, but little progress has been made in effecting their removal.

The diffusion of oxygen into zirconium is rapid at temperatures of 1000°C or higher. The diffusion rate of nitrogen into zirconium as a function of temperature is less than that of oxygen. The mobility of these gases, particularly oxygen, in the zirconium lattice at high temperatures suggests that the diffusion process could be reversed by application of a strong reducing agent, such as liquid calcium, in contact with the solid metal.

The validity of this reasoning has been supported by thermodynamic treatment, and demonstrated by observed decrease in hardness of treated zirconium, as well as by analytical determinations for oxygen before and after treating.

The removal of nitrogen by the same process is theoretically and practically impossible. It has been found that nitrogen is absorbed by zirconium during treating in amounts equivalent to those present in the calcium used. The pickup of nitrogen by zirconium, however, may be controlled as discussed later.

Since both oxygen and nitrogen contribute to the hardness and brittleness of zirconium, the ultimate result of heating in molten calcium depends upon the equilibrium concentrations in the following reactions.

[1] Manuscript received May 28, 1951. This paper prepared for delivery before the Washington Meeting, April 8 to 12, 1951.

(I) ZrO_2 (Solid solution in zirconium)

$$+ 2Ca(l) \rightleftharpoons 2CaO\ (s) + Zr.$$

(II) 2ZrN (Solid solution in zirconium)

$$+ 3Ca(l) \rightleftharpoons 2Zr + Ca_3N_2.$$

It is possible to eliminate reaction (II) by treating zirconium in calcium of very low nitrogen content, or by careful control of treating temperatures. This point is treated in more detail following a discussion of the theoretical and practical aspects of the process.

Theoretical Considerations

Oxygen equilibria.—The free energies, ΔF_0, for the reaction $ZrO_2 + 2Ca \rightleftharpoons Zr + 2CaO$ as a function of temperature with (1) liquid, and (2) gaseous calcium, are shown in Table I. Free energies and heats of formation are those given by Kelley (2) and Thompson (3).

The data in Table I indicate that the reaction becomes less favorable with increasing temperature. Below the boiling point of calcium the reaction appears to be more favorable with gaseous than with liquid calcium.

In comparing these data with experimental findings, the controlling factors for the reactions are the rate of diffusion of oxygen in the zirconium lattice and the solubility of calcium oxide in molten calcium.

The oxygen in zirconium is apparently in solid solution in the metal. With the following assumptions it is possible to calculate the oyxgen-zirconium equilibrium as a function of temperature:

1. CaO is insoluble in calcium, i.e., activity 1.
2. Dissolved ZrO_2 is the reactant at the Zr-Ca interface.

3. The reaction is specified by the equation ZrO_2 (dissolved) + 2Ca $\rightleftharpoons$ Zr + 2CaO.

Then for the molten treating, $K = 1/N_{ZrO_2}$, where N_{ZrO_2} is the mole fraction of ZrO_2 dissolved in solid zirconium.

For gaseous treating, $K = 1/N_{ZrO_2}P_{Ca}^2$ where P_{Ca} = pressure of Ca in atm.

From the relation $\Delta F_0 = -RT \ln K$ and the figures in Table I, minimum values for the oxygen content of the zirconium may be calculated. Based on these considerations, the equilibrium concentrations of oxygen in contact with molten calcium or calcium vapor are shown in Table II.

The calculated values for liquid and gaseous calcium are lower than those found experimentally in the temperature range 1000°–1300°C. At the boiling point of calcium, the values approach 0.02 per cent, which agrees closely with the determined minimum values for oxygen found by analysis of the treated metal[2].

TABLE I. *Free energies for the reduction of ZrO_2 with calcium*

Temp	Free energy ΔF_0 Cal/mole ZrO_2	
	(1)	(2)
°K		
1273	−34,000	−61,000
1572	−29,000	−40,000
1760 (bp Ca)	−27,000	−27,000

TABLE II. *Equilibrium concentration of oxygen in zirconium in contact with calcium*

Temp	Weight % oxygen dissolved in zirconium	
	Liquid Ca	Gaseous Ca
°K		
1273	0.00005	0.00003
1573	0.006	0.0035
1760	0.016	0.016

Nitrogen equilibria.—Free energies of the reaction of zirconium nitride with calcium may be calculated for the equation:

$$2ZrN + 3Ca \rightleftharpoons 2Zr + Ca_3N_2.$$

These energies as a function of temperature are given in Table III.

All the values are positive indicating that reaction would proceed from right to left. There appears to be little hope of removing nitrogen from zirconium by the calcium soaking process.

[2] It is possible that the actual oxygen content of the metal is lower than that found experimentally because of an uncertain blank in the analytical determination for oxygen.

Experimental

Extent of Oxygen Removal

For quantitative data on the removal of oxygen from zirconium by treating in molten calcium, samples of 0.125 in. diameter (Foote) zirconium rods were treated with pure oxygen to approximately 1 per cent oxygen by weight. This was accomplished by oxidation of the surface of the rods to the desired weight gain, and then homogenizing the oxide by vacuum treatment at 1300°C. The pieces were then cut in half, one portion being analyzed for oxygen by the chlorine distillation method (1), the other being treated in molten calcium at 1000°C for 1 hour. The treated halves were then analyzed for oxygen.

TABLE III. *Free energies for the reduction of zirconium nitride with calcium*

Temp	Free energy ΔF_0 Cal/mole Ca_3N_2	
	Liquid Ca	Gaseous Ca
°K		
1273	69,000	43,000
1573	71,000	61,000
1760	72,000	72,000

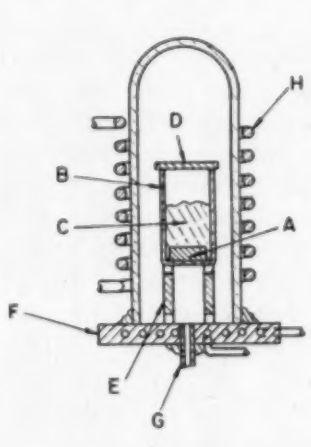

FIG - 1

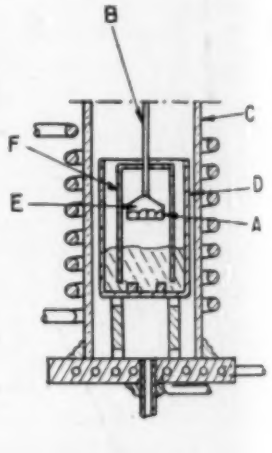

FIG - 2

FIG. 1. Apparatus for molten calcium treating. FIG. 2. Apparatus for treating in calcium vapor.

A cross section of the apparatus used is shown in Fig. 1. The solid zirconium, *A*, was placed in a molybdenum cup, *B*, tantalum lined to prevent alloying of the zirconium with molybdenum at the treating temperature. The metal was covered with calcium, *C*, and the molybdenum cover, *D*, set in place. The assembled container rested on an insulating support, *E*, and was surrounded by the Vycor jar which was sealed to the water-cooled brass plate, *F*. The Vycor jar was evacuated through the tubulation, *G*, and argon gas (99.7%) admitted to a pressure of about 0.75 atm. The molybdenum cup was then heated by high frequency, energizing the coils, *H*, until the calcium melted. The treating tempera-

ture was observed with an optical pyrometer. The oxygen content of the metal, before and after treating, is shown in Table IV.

The analytical results shown in Table IV are indicative of oxygen removal, and the hardness readings taken before and after treating are consistent with the analytical findings. The hardness data can be regarded as a fair correlation of hardness with oxygen as it has been established that little nitrogen is picked up at the above treating temperature.

Oxygen-Zirconium Equilibria Studies

The process was further studied to determine the effect of time and temperature of treating on the rate of oxygen removal. An attempt was made to establish the ultimate oxygen-zirconium equilibria as a function of these variables.

In the practical application of this process it appeared that zirconium containing over 0.5 per cent oxygen by weight need not be considered. Accordingly, a number of pieces of (Foote) 0.125-in. diameter rod were treated with oxygen in the range 0.02–0.46 per cent oxygen, and the oxide homogenized as previously described. The samples were cut in half and one part analyzed for oxygen. The remaining halves were then treated in molten calcium under the following conditions: (*a*) 5 hours at 1000°C, (*b*) 1 hour at 1300°C, and (*c*) 4 hours at 1300°C. The samples were then analyzed for oxygen giving the data shown in Table V.

TABLE IV. *Oxygen content of zirconium before and after calcium soaking at 1000°C*

Weight % oxygen, original	Weight % oxygen, after treating	% Total oxygen removed	Hardness,* original	Hardness, after treating
1.32	0.50	62.0	319	220
1.04	0.69	33.6	270	254
0.95	0.47	50.0	290	203

* Hardness figures are Vickers Pyramid Numbers.

The data for sample 9 suggests that the limiting oxygen equilibrium concentration is approximately 0.02 per cent, since 4 hours at 1300°C did not alter this figure (see Footnote 2).

It appears feasible to reduce the oxygen content of zirconium containing 0.5 per cent oxygen to a limiting value of approximately 0.02 per cent by treating in molten calcium at 1300°C for 5 to 6 hours or at 1000°C for a longer period.

From the data in Table V and from less extensive data for nitrogen, some idea of the rates of reactions (I) and (II) has been obtained. Reaction (I) proceeds moderately fast at temperatures in the range 1000°–1300°C. Reaction (II) proceeds very slowly from right to left at temperatures not exceeding 1000°C, but is quite rapid at 1300°C. It is, therefore, possible to remove oxygen without further contaminating the zirconium with nitrogen, by treating at temperatures not in excess of 1000°C.

By treating zirconium in molten calcium at 1300°C it is possible to utilize the process for the purification of calcium with respect to nitrogen, zirconium nitride being formed in amounts equivalent to those present in the treated calcium as calcium nitride.

Oxygen Removal by Gas Phase Reaction

In addition to experiments concerning treatment in molten calcium, additional investigations, although less extensive, were carried out on treating in calcium vapor. Preliminary work indicated that oxygen may be appreciably reduced by such treatment.

The oxygen-zirconium equilibria data for such a system has not been evaluated, and the proof of removal rests on the observed decrease in hardness found after treating in calcium vapor for 1 hour at 1000°C. This amounted in one experiment to a drop of 40–50 points VPN.

TABLE V. *Oxygen removal from zirconium by molten calcium treating*

Treatment			Oxygen content weight %		Fraction removed
Sample No.	Temp °C	Time, hrs	Original	Final	
1	1000	5	0.06	0.02	0.67
2	1000	5	0.06	0.02	0.67
3	1000	5	0.28	0.02	0.93
4	1000	5	0.46	0.15	0.67
5	1300	1	0.07	0.02	0.71
6	1300	1	0.14	0.02	0.86
7	1300	1	0.20	0.02	0.90
8	1300	1	0.37	0.08	0.78
9	1300	4	0.02	0.02	0.00
10	1300	4	0.34	0.02	0.94
11	1300	4	0.45	0.07	0.85

The advantage of using calcium vapor in place of molten calcium is the avoidance of the adverse nitrogen reaction which results from the residual nitrogen content of calcium used for treating. Thus, it is unnecessary to purify calcium with respect to nitrogen for the gas phase reaction, which is desirable in the molten treatment when operating at temperatures in excess of 1000°C.

Vapor treating is more difficult experimentally than molten treating, since it is necessary to resort to a closed system. Preliminary experiments indicate that the kinetics of the reaction are less favorable than when using molten calcium. Experimental equipment for vapor treating was comprised of a Vycor bottle and assembly generally similar to Fig. 1. Important modifications are shown in Fig. 2. Referring to this figure, the calcium is placed in an

iron or molybdenum container, *D*. Iron containers are satisfactory for temperatures up to 1000°C, but molybdenum is desirable for the higher temperatures. An inverted iron or molybdenum container, *F*, forms a molten seal with the calcium. The material to be treated, *A*, is placed in the tantalum basket, *F*. The molybdenum rod, *B*, extends through a tubulation (not shown in the diagram) in the Vycor bottle, *C*, and thence through a rubber seal, to permit raising or lowering the basket. The source of energy is a high frequency coil, the inner cup being heated by radiation from the outer cup, *D*. Treating was in 99.7 per cent argon gas at slightly less than one atmosphere.

TABLE VI

Sample	VPN before treating	VPN after treating	Drop VPN
1	230	115	115
2	230	157	73
3	188	136	52
Avg	216	136	80

For molten calcium treating using the apparatus shown in Fig. 1, it is necessary to dissolve the calcium out of the container after each run. To avoid this, the apparatus shown in Fig. 2 may be modified by removal of the inverted cup. Samples of zirconium may then be lowered in the basket into the molten calcium and raised after treating. The operation may be repeated with a small loss of calcium.

This modification also permits purification of the calcium with respect to nitrogen. In this case, the basket containing scrap zirconium is lowered into the molten calcium and the residual nitrogen in the calcium is transferred to the zirconium scrap at a temperature sufficiently high to cause reaction (II) to proceed from right to left. The scrap is raised out of the bath and replaced with zirconium to be processed. The operation is then repeated for oxygen removal. The process thus may be used for the purification of calcium from nitrogen as well as for the removal of dissolved oxygen from zirconium.

The effect of treating zirconium of a relatively low oxygen content in calcium of a low nitrogen content, purified as described above, was investigated, and the hardness of the metal before and after treating was determined. In this work, scrap zirconium was soaked in molten calcium containing 370 ppm nitrogen. After treating for two hours at 1300°C, the nitrogen content of the calcium dropped to 15 ppm.

Three different samples of calcium-reduced zirconium (sintered and worked bar stock) were treated in the low nitrogen calcium for two hours at 1300°C. Standard Vickers hardness readings were taken before and after treating. The results are shown in Table VI.

The final average hardness is a little higher (25–50 VPN) than commercially available iodide zirconium, and about the same as the best metal produced by other processes.

ACKNOWLEDGMENT

Permission to publish the information contained in this paper by the Atomic Energy Commission, New York Operations Office, is appreciated.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the JOURNAL.

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Arc Melting of Zirconium Metal[1]

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ABSTRACT

In arc-melting zirconium metal with a tungsten electrode, tungsten appears in non-uniform amounts throughout the ingot. To eliminate this, the use of consumable electrodes of zirconium sponge is proposed. All early attempts to use sponge zirconium electrodes were unsuccessful due to instability of the arc. This problem was solved by stabilizing the arc with a small amount of magnesium metal added to the zirconium sponge used in making up the electrodes. A water-cooled copper sleeve was used as a melting section in the arc-melting furnace. Melting was done under an inert atmosphere of argon or helium. Metallographic and radiographic studies show the finished ingots to be sound.

Introduction

It has been reported that zirconium may be melted satisfactorily in graphite crucibles in vacuum or in a noble-gas atmosphere (2–5). Ingots so produced usually are contaminated with carbon to the extent of about 0.2 per cent. Although the presence of this amount of carbon is not objectionable for most uses, it was found necessary for certain applications to develop melting methods that would give no appreciable contamination. Arc melting offers the greatest promise along this line.

Arc fusion of metals has been practiced for many years. Espe and Knoll (6) report that Von Bolton of Siemens & Halske arc-melted tantalum scraps in a glass-enclosed arc furnace for many years. Kroll (1) employed a similar furnace made of steel, using a tungsten electrode for melting titanium in vacuum. Weiss (7) employed two consumable electrodes in attempting to prepare pure zirconium by arc-melting zirconium-aluminum alloys in vacuum. He also melted consumable electrodes of tungsten (8). Parke (9) made molybdenum ingots in a water-cooled, copper sleeve, using a consumable electrode that was made up inside the furnace. This marked an advance over the established technique, although Clauser (10) had been making special alloy steels in a sleeve furnace before this time. Another important step was the advent of arc melting under noble gas as reported by Simmons (11). This made possible a number of simplifications and improvements not attainable in vacuum furnaces. Herres (12) melted titanium on a large scale by similar methods.

Preliminary Work

Several tests were conducted in an effort to devise an arc furnace that could melt at least 100 pounds (45 kg) of metal a day. Melting with a tungsten tip was not considered suitable, as it had been noted (2) that zirconium invariably splashes onto the electrode tip and drops back contaminated with tungsten. Although the percentage of tungsten in the ingot is low, it is present as spots of rather high concentration that cause flaws in the ingot. Graphite tips were found to give the same trouble. After a short time in service, they became coated with a layer of zirconium metal rich in zirconium carbide, which contributed about 0.1 per cent carbon to the ingot. Zirconium carbide tips (2) prepared by impregnating sintered compacts of zirconium carbide with zirconium metal gave a satisfactory arc, but they also produced ingot containing about 0.1 per cent carbon. Carbide tips also tended to form accretions of splashed metal, which restricted movement of the electrode in the furnace.

Since all of the above difficulties are due to spattering of the metal, an attempt was made to outgas the metal by evacuating at high temperature (1). This method was found to be impractical, as it requires a very high vacuum with temperatures from 1200° to 1600°C and gives erratic results. Metal that had been held at a temperature just below the melting point for one hour spattered badly on melting. The cost and difficulties of treating tonnages of metal in this way are strong deterrents to this procedure.

Experimental

Results of these tests indicated that consumable electrode melting offered the best possibility of producing ingots of the required purity. It was apparent that the cost and time involved in producing electrodes would have prime importance. By using a direct-current arc in which the movable electrode was made the cathode, it was expected that enough heat would be generated in the anode pool to permit

[1] Manuscript received April 13, 1951. This paper prepared for delivery before the Washington Meeting, April 8 to 12, 1951.

melting of additional chopped metal, thereby reducing the electrode requirements. Crude zirconium sponge is rather difficult to chop or crush to small size, so it was difficult to add metal to the pool. This problem was overcome by constructing a rectangular steel feeder box 12 inches (30.5 cm) square and 10 inches (25.4 cm) high, with a 2-inch (5 cm) diameter opening in one end of the box communicating with the melting chamber of the furnace. Feeding was accomplished by pushing pieces of zirconium into the arc by means of a rod manipulator through a rubber glove clamped to a hole at the opposite end of the box. Feeding was controlled by observation through a 6- by 8-inch plate-glass window in the top of the feed box.

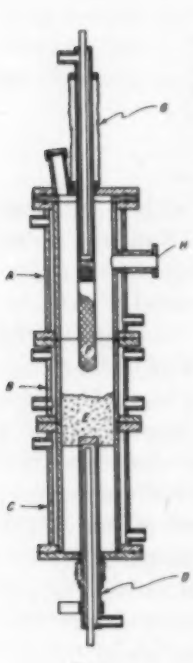

FIG. 1

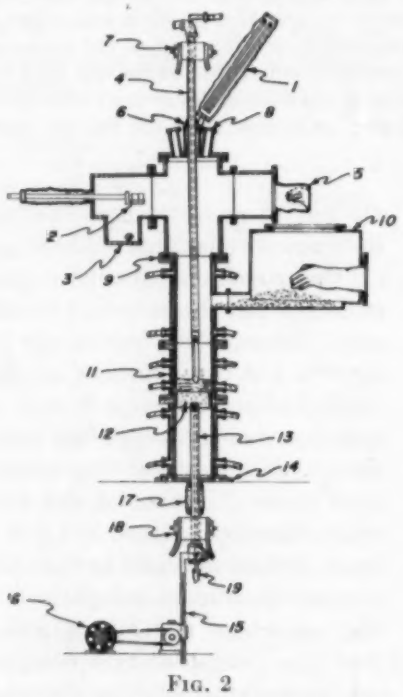

FIG. 2

FIG. 1. Arc furnace. *A*—feeding section, *B*—melting section, *C*—extraction chamber, *D*—retractor, *E*—zirconium starter plug, *F*—zirconium electrode, *G*—electrode holder. The feed box was attached at *H*.

FIG. 2. A 4-inch (10 cm) diameter production furnace. (*1*) Rubber container for new electrodes, (*2*) stub-removing wrench, (*3*) well for stubs, (*4*) electrode holder, (*5*) electrode charging glove, (*6*) bicycle inner tube, (*7*) power lugs, (*8*) eyepiece, (*9*) electrical insulation, (*10*) feed box, (*11*) melting chamber, (*12*) zirconium starter plug, (*13*) ingot extractor, (*14*) base, (*15*) geared retractor, (*16*) variable-speed motor, (*17*) bicycle inner tube, (*18*) power lug, (*19*) water cooling on extractor.

Electrodes were made up by pressing 1-inch (2.5 cm) lumps of zirconium sponge into 3-inch (7.6 cm) diameter cylindrical briquets under a pressure of 20 tons per square inch (280 kg/cm^2). A 6-inch (15 cm) stack of briquets was placed in a piece of $\frac{1}{2}$-inch (12.7 mm) wall-seamless-steel tubing, and steel caps were arc-welded over the ends. These sheathed briquets were forged and rolled at 850°C to square bars. The sheathed bars were opened on a planer and the sheaths removed, leaving a compressed zirconium rod approximately 1 inch (2.54 cm) square. These rods were cut to 24-inch (61 cm) lengths and threaded for attachment to the electrode holder. Extruded sponge bars might be more economical, but suitable extrusion equipment was not available.

For test purposes, a small arc furnace was constructed, as shown schematically in Fig. 1.

Test bars were made from selected lots of zirconium sponge, and trial runs were made to determine the power requirements of the furnace. Before operation, the furnace was evacuated to a pressure of less than 1 mm Hg and back-filled with argon. An input of 800 amperes at 40 volts consumed the electrode, but the arc was erratic; hence little metal was consolidated into the ingot. Variations in power input failed to improve the melting characteristics. It appeared that, under these conditions, zirconium had insufficient vapor pressure to support a stable arc. A high-frequency wave was superimposed on the d-c input; this facilitated starting the arc but did not improve its stability. The difficulty was corrected by adding magnesium to the sponge prior to the briquetting step.

Consumable electrode sponge bars containing magnesium produced a quiet, steady arc that could be maintained with an input of 1500 amperes at 20 volts. A small, spherical area of ionized magnesium vapor established itself between the electrode and the molten pool, which quickly grew to 4 inches (10.2 cm) diameter by $\frac{3}{4}$-inch (1.8 cm) depth. The magnesium-containing bars were consumed very slowly in comparison with bars from the same lots of metal without added magnesium. When the molten pool was well established, chopped zirconium was dropped in as rapidly as it could be melted. Several ingots were made from equal weights of electrode and chopped metal.

Several hundred pounds of ingot were produced for metallographic and fabrication studies. The finished ingots were $3\frac{1}{2}$ inches (8.9 cm) in diameter by 10 to 12 inches (25.4 to 30.5 cm) long and weighed up to 30 pounds (13.6 kg). Radiographs showed a layering effect after each replacement of the electrode. Metallographic examination indicated, as would be expected, a weld-upon-weld structure, with varying degrees of crystal refinement in haphazard horizontal planes. The hardness varied, depending upon the particular lot melted; the minimum hardness was R_b 52. Residual magnesium in the ingot was low despite the additions made for arc stabilization. The results of five selected tests are summarized in Table I.

Production in this furnace was low, as it was necessary to allow the ingot to cool, open the furnace, pump down, and refill with argon each time a new electrode was installed.

A 4-inch (10 cm) diameter production furnace, which is shown in Fig. 2, has since been placed in operation. This incorporates a device for feeding additional electrodes into the furnace from an automobile inner tube (*1*). Stubs of consumed electrodes are unscrewed by means of a geared device (*2*) and deposited in a well (*3*). The new electrode is lowered through a hole in the lid and screwed into the electrode holder (*4*) by means of a rubber glove (*5*). A flexible seal (*6*) made from a length of bicycle inner tube allows the water-cooled electrode holder to be moved. Electrical connections are shown at (*7*) and (*18*). The arc is observed through a Pyrex eyepiece (*8*). The furnace is electrically insulated by means of a Bakelite ring (*9*). Vacuum seals are provided by $\frac{1}{4}$-inch (6.3 mm) diameter molded-rubber rings. The furnace is evacuated and filled with argon through an opening in the feed box (*10*). The melting section (*11*) has only a $\frac{1}{16}$-inch (1.6 mm) space around the pure copper melting liner, so the cooling water passes through at high velocity. A starter plug (*12*) of zirconium is threaded to the extractor (*13*), which passes through the base (*14*) to a geared mechanical device (*15*) driven by a variable-speed motor (*16*). The extractor is vacuum-sealed by a length of bicycle inner tube (*17*) and has a power connection (*18*) and water connections (*19*).

Most of the electrical current is conducted by the starter plug and extractor; the ingot remains free at all times for either continuous or intermittent extraction, but no arcing occurs to the copper liner. The arc may be extended to 2 inches (5 cm) length, while the electrode is moved to within $\frac{1}{8}$ inch (3.2 mm) of the furnace wall without side arcing. Melting liners remain usable until accidentally struck by the electrode. No difficulties have arisen from perforation of the water jacket.

One operator with an assistant can produce a 40-pound (18 kg) ingot in 50 minutes, using 20 pounds (9 kg) of electrode and 20 pounds (9 kg) of feed. The assistant controls the rate of feed and extraction of the ingot and maintains the combined output of 7 d-c welding generators at 1800 amperes, with 20 volts across the arc. Actual melting requires about 1 kwhr of power per pound of rough ingot. During an 8-hour shift two men now produce about 150 pounds (68 kg) of rough ingot.

Ingots are normally scalped about $\frac{1}{4}$ inch (6.3 mm) deep on the lathe giving an 80 to 85 per cent recovery from a 4-inch (10 cm) diameter ingot. The cold shuts encountered with the first furnace have been practically eliminated by the quick replacement of electrodes possible with the new model. Soundness of metal was determined by sawing the ingots vertically on the mid-line, polishing, and etching deeply with hydrofluoric acid.

A larger furnace will soon be ready for testing automatic control of electrode movement and feeding.

TABLE I

Zr sponge Lot No.	Mg added %	Ingot produced	% Mg residual
75A	0.02	S-950	<0.005
76A	0.05	S-945	<0.005
74A	0.13	S-953	<0.005
64A	0.26	S-966	<0.005
71A	0.45	S-947	<0.005

Summary

It has been shown that consumable electrode arc melting of zirconium metal can be done on a small-scale production basis. Larger ingots of uniform structure and high purity probably can be made by simply extending the length of the furnace, as required. The diameter of the ingot might be increased by using three or more electrodes. Impurities in the ingot are accounted for by those present in the metal used; some of the more volatile impurities are actually removed by the heat of the arc.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the JOURNAL.

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Effects of Working on the Properties of Molybdenum[1]

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ABSTRACT

Heat-treated unworked molybdenum made by the powder metallurgy process has an ultimate strength of about 60,000–70,000 psi and an elongation of usually less than 1 per cent. Upon rolling at suitable temperatures, however, the hardness increases and, under some conditions, the strength and ductility are greatly improved in the direction of the metal flow brought about by the working.

There is no improvement in strength or ductility in the compressive direction, that is, the direction in which flow does not take place.

Introduction

The properties of worked molybdenum are generally given without mention of the amount of previous working or direction in which the properties are measured. It is well known that molybdenum drawn into a fine wire possesses greater strength than larger rod or slab rolled to a lesser degree. During the fabrication of molybdenum, however, many steps are involved when the molybdenum may initially be rolled above recrystallization temperatures and later worked at lower temperatures at which recrystallization does not occur. Molybdenum fabricated at temperatures considerably above the recrystallization temperature will show grain growth with substantially no increase in hardness or strength. Molybdenum worked below recrystallization temperatures develops a finer grain structure with an increase in strength and hardness depending upon the amount of working that has been done.

Previous data reported by Marden and Wroughton (1) were obtained on commercially available material. During fabrication, however, this material was subjected to repeated working and annealing. In order to eliminate the variables present in the repeated fabricating and annealing cycles, the present data were obtained on a wedge whereby the reduction could be varied in a single rolling pass at a given temperature. This procedure was used by Chipizhenko (2) in determining plasticity by rolling tests.

Attention is called to the fact that the properties in the direction of metal flow are different from those measured in the thickness or compressive direction of rolled strip.

Procedure

The use of a wedge machined from a solid ingot allowed varying reductions to be made on material possessing initially the same grain size and density, and having the same rolling temperature. Solid ingots of molybdenum were first prepared by the methods of powder metallurgy, i.e., pressing of metal powder and sintering to a substantially solid ingot. Two wedges, 13 in. long by 1½ in. wide by ⅜ in. thick at the thinner end, were machined with a taper of 0.106 in. per in. of length (Fig. 1), and lines were inscribed at ½-in. intervals on both sides along the length. These were rolled to ⅜ in. thickness at 1200°C in a single pass in a 21 in. x 42 in. rolling mill. One wedge was air-cooled after rolling and the other was annealed for 1 hour at 950°C. Measurements of the height of the wedge after rolling at each of the scribed marks, when compared to the original height at the same points, gave a measure of the degree of height reduction. Hardness measurements were made across the surface of the rolled wedges at positions located by the previously scribed lines. Using the lines also as centers, round tensile specimens, 1¼ in. long by 0.187 in. diameter, were prepared and tensile tests made of the properties transverse to the rolling direction.

In order to show what relation these transverse properties would have to the properties in the longitudinal rolling direction and to the properties in the thickness or compressive direction, round tensile specimens, ⅛ in. diameter by 1 in. long, were cut from a factory-rolled slab 1 in. x 2½ in. in cross section. Six specimens were tested in each of the three directions: longitudinal, transverse, and thickness.

Results

The sintered ingots, prior to rolling, had a hardness of 150 VPN, a strength of 60,000–70,000 psi, and were quite brittle. After a single rolling pass on the wedges, the initial properties increased with increasing reduction in both the as-rolled and annealed condition as shown in Fig. 2. In each case, the hardness increases rapidly at first with increasing reduction

[1] Manuscript received April 27, 1951. This paper prepared for delivery before the Washington Meeting, April 8 to 12, 1951.

up to about 25 per cent reduction. Above 25 per cent reduction, the hardness increases more slowly. The hardness of the annealed and as-rolled material is substantially the same at the lower reduction values, but the hardness of the annealed material approaches a lower maximum value than that of the as-rolled material.

The transverse strength of the annealed material rapidly approaches a substantially constant value at reductions of the order of 25 per cent. The strength of the as-rolled material, on the other hand, increases

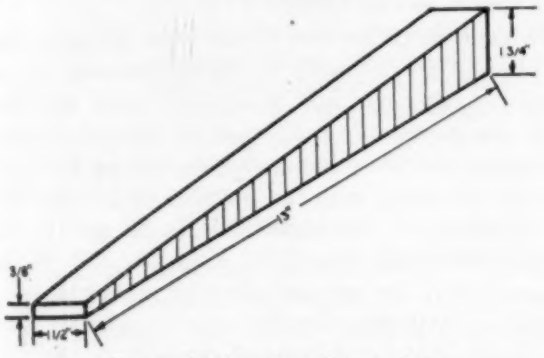

FIG. 1. Wedge-shaped test piece

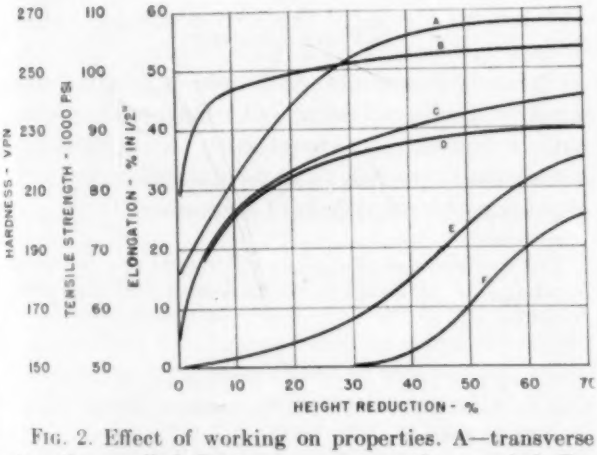

FIG. 2. Effect of working on properties. A—transverse strength, as-rolled; B—transverse strength, annealed; C—hardness, as-rolled; D—hardness, annealed; E—transverse ductility, annealed; F—transverse ductility, as-rolled.

much more slowly with increasing reduction, approaching a substantially constant value at about 40 per cent reduction.

The ductility of molybdenum, expressed as per cent elongation, results in an S-shaped curve when plotted against degree of reduction. The ductility first increases slowly, suddenly increases greatly, and then slowly rises as reduction is increased. The curves for the as-rolled and annealed material are substantially parallel with higher amounts of reduction. At low reductions, the annealed material possesses some ductility, whereas the as-rolled material is brittle. The points at which the ductility begins to increase rapidly corresponds to the point at which the tensile strength begins to approach a constant value, namely 25 per cent reduction for the annealed material and 40 per cent reduction for the as-rolled material.

The elongation-reduction curves show essentially the effect of working on the lowering of the transition temperature of molybdenum during a slow tensile test. To obtain maximum ductility at room temperature, it would be necessary to reduce the height of

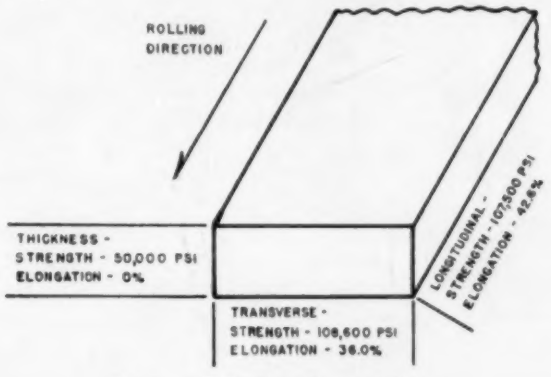
ROLLING DIRECTION
THICKNESS - STRENGTH - 50,000 PSI ELONGATION - 0%
LONGITUDINAL - STRENGTH - 107,500 PSI ELONGATION - 42.8%
TRANSVERSE - STRENGTH - 108,600 PSI ELONGATION - 36.0%

FIG. 3. Directional properties

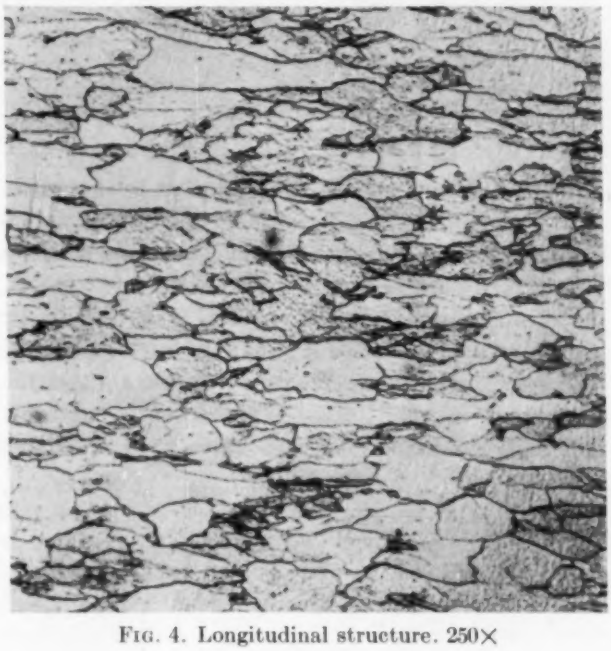

FIG. 4. Longitudinal structure. 250×

the ingot by 60 to 70 per cent, whether in the as-rolled or annealed condition. With intermediate reductions of 30 to 60 per cent, however, some ductility can be obtained. Below 30 per cent reduction, ductile material was not produced.

These curves are average curves drawn through values of single tensile tests and, therefore, do not indicate exact values but trends. In addition, as the amount of working in a given piece is increased, the recrystallization temperature is decreased. Thus, for high values of reduction some instantaneous recrystallization may occur at the rolling temperature

used and result in some variation in properties. Also, roll slippage and lifting may occur in rolling of wedges causing some variation in properties in the finished piece.

The test results on these wedges have all been given in the transverse or width direction. Fig. 3 shows a factory-rolled slab reduced 56 per cent in

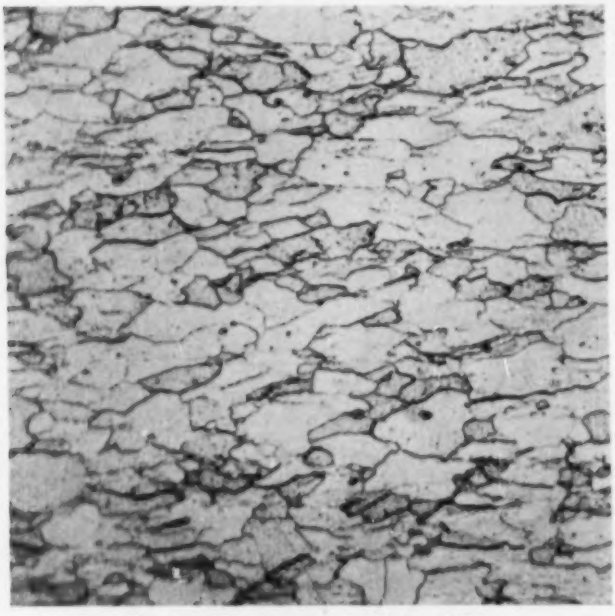

FIG. 5. Transverse structure. 250×

height[2] which illustrates the variation in properties in the three directions. The longitudinal and transverse strengths are substantially equal whereas the strength in the thickness direction is of the same order of magnitude as the strength of a sintered ingot. However, the elongation is greater in the longitudinal direction than in the transverse direction, and the elongation in the thickness direction is zero. In flat rolls, an ingot elongates considerably, widens to some extent, and is decreased in thickness. The grains of the material are elongated both in the longitudinal and transverse directions as shown in Figs. 4 and 5. They are, however, compressed in the thickness direction. It is apparent that worked molybdenum develops strength and ductility in the directions in which the grains are elongated or in the directions of metal flow. No increase in strength or ductility is noted in the direction along which the compressive force is applied.

[2] Reduction accomplished in four passes at 1200°C with reheating between passes.

CONCLUSIONS

In general, reductions of the order of more than 30 per cent are necessary to produce material having hardness, strength, and reasonably good ductility. It is also necessary, in the case of worked material, to report the direction in which testing has been carried out along with the physical properties. This is mandatory if the material is to be used in any strength-carrying capacity, since it will be no stronger than the weakest direction unless design is correlated with directionality to overcome the inherent weakness in strength and ductility in the compressive direction.

ACKNOWLEDGMENT

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Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the JOURNAL.

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The Uranium-Carbon System[1]

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ABSTRACT

An investigation of the uranium-carbon system has been made and a constitutional diagram drawn on the basis of melting point, x-ray, and metallographic data. Three carbides of uranium have been detected and identified: UC, U_2C_3, and UC_2. No compounds have been found containing a carbon content higher than that of UC_2. UC and UC_2 are completely soluble in each other at elevated temperatures, forming a solid solution. The solid solution phase cannot be retained on cooling to room temperature in alloys containing between about 5.0 to 9.0 weight per cent carbon. A Widmanstätten type of precipitation takes place on cooling, leaving either UC precipitated in a UC_2 matrix or vice versa, depending on the carbon content of the alloy. In alloys containing above about 9.0 weight per cent total carbon, UC can quite effectively be retained in solid solution by quenching from temperatures above about 1800°C.

Introduction

A carbide of uranium was reported by Moissan (1) in 1896 to which the formula U_2C_3 was assigned. It was later shown by careful chemical and metallographic investigation by others (2) that the composition of carbide made in a manner similar to that used by Moissan is correctly expressed by the formula UC_2. In 1931, Hägg (3) reported the crystal structure of UC_2 to be body-centered tetragonal of the LaC_2 type. This was verified by later investigations (4–7).

The monocarbide, UC, was prepared and identified at (4, 5) Iowa State College in 1943 as having a face-centered-cubic, NaCl-type crystal structure, which has been checked by others (6). The workers at Iowa State College also proposed a phase diagram in which U_2C_3 was hypothesized as a high-temperature phase existing above 2000°C and having broad solubility limits (4). The crystal structure of U_2C_3, which was found (8) to exist as a stable compound below about 1800°C, was determined to be body-centered-cubic with a unit-cell dimension of $a_0 = 8.088 \pm 0.001$ Å. U_2C_3 is isostructural (9) with Pu_2C_3.

This paper presents the results of an investigation of the uranium-carbon system, the purpose of which was to establish the constitutional diagram of this system.

Experimental Procedure and Equipment

Preparation of Alloys

The melting stock used for the alloys in this investigation was made by reacting an intimate mixture of uranium oxide with monatomic carbon (Norblack) to produce carbon monoxide and uranium dicarbide. The charge was contained in a thick-walled graphite crucible which was heated by induction power from a motor-generator set. The reaction, as indicated by a flame of burning carbon monoxide emitted from the crucible, proceeded at a useful rate at about 1900°C. The temperature increased as the reaction neared completion. The end point of the reaction is quite critical in that it is necessary to stop heating as soon as the carbon monoxide flame has died down. If not immediately stopped, an excessive amount of carbon from the crucible will dissolve in the molten uranium dicarbide. Scrap uranium carbide can be reclaimed by merely adding it to the oxide-carbon mixture. Master alloys produced by this technique have contained between 10 and 12 weight per cent carbon. Ingots weighing up to 75 pounds have been made.

The alloys, of various carbon contents, used for this investigation were made by an application of an arc-melting technique developed at Battelle. The furnace has been described in detail elsewhere (10). Early melts, using a tungsten electrode, gave excessive tungsten contamination. A graphite electrode was substituted because allowance could be made for carbon pickup from the electrode, making possible accurate control of carbon content. Both helium and argon were used as the furnace atmosphere.

The master alloy, described above, was mixed with pure uranium chips to produce melting stock of the desired composition. This stock was charged continuously into the furnace during the arc-melting operation. All of the ingots thus made were crushed and remelted at least once to insure greater homogeneity. The usual variation in the total carbon content was ±0.2 weight per cent from the reported

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average. Final ingots were about 2¼ in. in diameter, ⅝ to ¾ in. high, and weighed about 500 grams each.

Analysis

In order to check the homogeneity of the arc-melted ingots, chemical analyses of the total and free-carbon contents were run. The determination of total carbon was made by essentially the same method (11) as used in determining carbon in iron or steel. However, because of the relatively high carbon content, a smaller sample size (about 0.7 g) was used and the burning time was increased to 15 minutes. No flux was needed and 1260°C was a sufficiently high burning temperature.

Free carbon was determined by a modification of the method used for free carbon in iron (11). Here a somewhat different technique was used because, in the hydrolysis of the uranium carbide, a wax is formed as well as hydrocarbon gases. The essential steps in this procedure are as follows:

1. Approximately 2 grams of finely divided sample are required per determination.
2. The sample is hydrolyzed in 1:1 HCl until no uranium carbide is left unreacted.
3. The resulting mixture of graphite and wax is filtered on a pad of ignited asbestos.
4. The asbestos pad is washed successively with water, ethyl alcohol, and ethyl ether. The ether wash is continued until all the wax is dissolved and washed free of the asbestos mat.
5. The asbestos mat containing the residual graphite is transferred to a combustion boat and dried at 110°C for at least 30 minutes.
6. The asbestos and graphite is then burned in the usual combustion apparatus at about 1260°C for 15 minutes.

Heat Treating in Vacuum

The furnace used to heat-treat the uranium carbide samples in vacuum consisted of a closed-end, vitreous-silica furnace tube mounted vertically. The furnace tube was attached to the vacuum system by means of Apiezon W wax.

The vacuum was supplied by means of a type MC-275 all-metal, vertical, high-speed oil-diffusion pump backed by a Welch Duo Seal, type-1405-B forepump. Standard 4-in. pipe fittings were used wherever possible and the vacuum was measured by means of thermocouple gauges in the high-vacuum and forepump sections of the system.

Heating was accomplished by high frequency induction, the power being supplied by a 30 kw Lepel converter.

A sample of uranium carbide to be heat-treated was placed on chips of uranium carbide of similar composition in a graphite crucible. The crucible was placed inside of a graphite heater which was thermally insulated with 60-mesh graphite powder retained by an Alundum or beryllia thimble (12). This whole assembly was then set on Alundum sand inside the vitreous-silica furnace tube. After the furnace was evacuated to a pressure of less than 5 microns of mercury, heating of the sample was begun.

After heating, the uranium carbide test specimens were cooled in one of three manners:

1. The power from the converter was shut off and about 100 grams of tin were dropped into the crucible from a storage magazine. The vacuum was then broken by admitting high-purity argon and the crucible containing the uranium carbide and molten tin was removed from the furnace and quenched in a pail of cold water. The sample was cooled to room temperature in 45 seconds or less by this technique which, in the present paper, is referred to as water quenching.
2. The power was turned off and the sample allowed to cool in the crucible, in vacuum, at the normal cooling rate of the furnace (100° to 150°C per minute). This method of cooling has been designated as furnace cooling.
3. The temperature of the furnace was reduced by detuning the converter slightly at regular intervals, thus allowing the sample to cool very slowly in the crucible in vacuum at a rate of cooling of 15° to 30°C per minute. This method of cooling has been called very slow cooling.

Determination of Melting Points

The melting points of the alloys below 4.8 weight per cent carbon were checked by melting pure uranium in graphite crucibles in vacuum. The melts were then held at various predetermined temperatures above the melting point of pure uranium for one hour. This time was sufficient to reach the solubility limit of carbon in uranium for the temperature being checked. The alloys containing more than 9.0 weight per cent carbon were saturated with carbon in a similar manner by heating UC_2 above its melting point. The centers of the resulting ingots were analyzed to determine the equilibrium carbon content at the holding temperature. Each determination produced a point on the liquidus line of the diagram.

The determination of the solidus and liquidus line from 4.8 to 9.0 weight per cent carbon was done by placing a graphite ring, about ¼ in. thick, inside a regular graphite crucible. A piece of uranium carbide of known carbon content was then chosen which had a sharp peak or ridge protruding from the sample. This irregular piece was set upon the ring and, after the system had been evacuated, heating was begun.

The temperature at which the ridge or peak of the sample rounded off was called the solidus point. The liquidus point was the temperature at which the sample lost its shape and fell into the bottom of the crucible through the graphite ring. Temperature measurements were made by means of a Pyro optical pyrometer equipped with a high-temperature filter. The observed temperature, which was read through two Pyrex glasses, was corrected by suitable calibration of the pyrometer[2]. Black-body conditions were approached since the crucible was $\frac{3}{4}$ in. in diameter and about $3\frac{1}{2}$ in. deep.

Preparation of Samples for Metallographic Examination

The best method found for preparing samples of uranium carbide for metallographic examination consists of the following steps:

1. The sample to be examined, which is quite brittle, can usually be removed by chipping with a chisel and hammer.

2. After mounting in Bakelite, it is rough ground under light pressure on a new 240-grit continuous silicon carbide belt in a stream of water.

3. Hand grinding is continued under light pressure successively on 400- and 600-grit wet or dry waterproof Tri-M-ite[3] silicon carbide papers with water on the papers.

4. Final polishing is done with Linde "B" alumina abrasive suspended in water on Forstmann's cloth under light pressure. A wheel speed of about 1250 rpm is used.

5. The polished sample is etched by dipping in an etchant consisting of equal volumes of nitric acid, acetic acid, and water. In some cases, the volume of water is halved to increase the speed of the etchant. An etching time of 5 to 30 seconds is usually adequate.

This etchant is of the staining type and the uranium monocarbide is stained more readily than uranium sesquicarbide or uranium dicarbide. A more detailed description of the etching characteristics of these materials has been given in another paper (8).

[2] Pyrometer was calibrated for reading through two Pyrex glasses against a tungsten-filament lamp over a range of temperatures up to about 1800°C. The temperature of the lamp could be varied by changing the voltage supplied to the filament. The range of the pyrometer was then extended by means of the following equation based on Wien's law (13):

$$\frac{1}{T} - \frac{1}{T_A} = K,$$

where T is the true temperature in absolute degrees,
T_A is the observed temperature in absolute degrees,
K is a constant which may be evaluated by any pair of true and apparent temperatures. Then any other apparent temperature, T_A, may be converted to its corresponding true temperature, T.

[3] Minnesota Mining and Manufacturing Company, St. Paul, Minnesota.

Constitutional Diagram

The constitutional diagram for the uranium-carbon system, shown in Fig. 1, has been constructed from metallographic, x-ray, and melting-point data. Three compounds have been identified in this system: uranium monocarbide, UC (4, 5), uranium sesquicarbide, U_2C_3 (8), and uranium dicarbide, UC_2 (3, 5, 6).

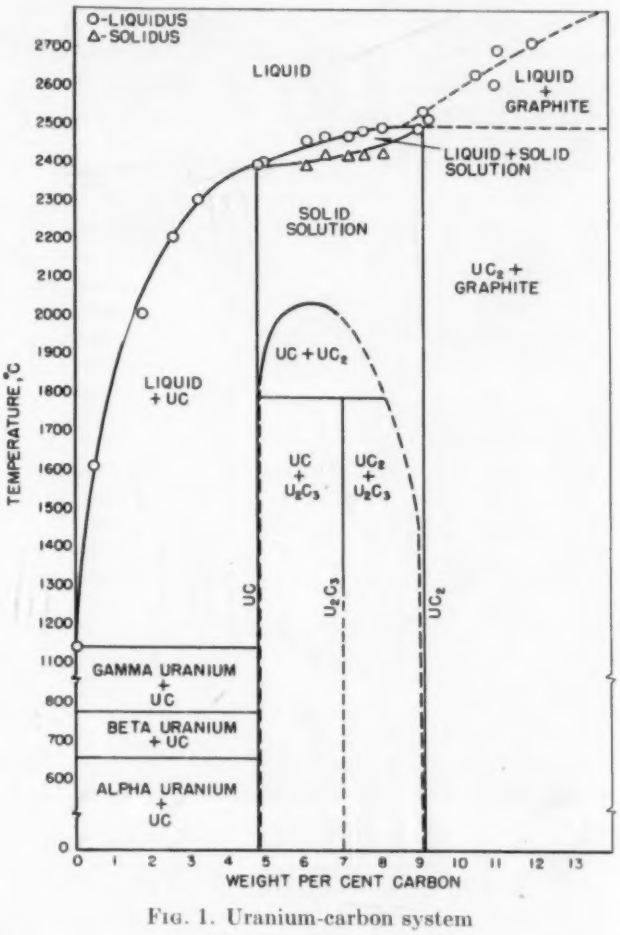

FIG. 1. Uranium-carbon system

The melting point of uranium monocarbide lies between 2350° and 2400°C and that of uranium dicarbide between 2450° and 2500°C. Uranium sesquicarbide (8) is stable below about 1775°C and, once formed, is probably stable to subzero temperatures. It decomposes to UC and UC_2 when heated to temperatures above 1800°C.

Below 4.8 weight per cent carbon, a mixture of UC and uranium exists. The uranium is in the alpha, beta, or gamma form, depending on the temperature. The transformation temperatures determined by others (14) for pure uranium apparently are constant across the diagram to the composition of UC at 4.8 weight per cent carbon. Slight solid solubility of carbon in uranium has been reported (4).

The solidus and liquidus lines up to 12 weight per cent carbon were determined by methods previously described and the experimental data are listed in Table I.

Fig. 2 shows the variation in the microstructure from the composition of UC to that of UC_2. The sample was taken at the interface of an ingot of uranium carbide and its graphite crucible which had been furnace cooled. The UC (dark etching) with UC_2 precipitated along certain crystallographic planes appears at the left side of the photomicrograph, while the UC_2 (light etching) with a UC precipitate is shown at the right. U_2C_3 is not present in this sample, since it does not form on cooling from the melting temperature (8).

TABLE I. *Melting points of uranium-carbon alloys*

Total carbon weight per cent	Solidus point °C	Liquidus point °C
0.48		1600[2]
1.74		2000[2]
2.6		2200[2]
3.23		2300[2]
4.88		2390
4.94		2395
6.11	2380	2450
6.60	2410[1]	2455[1]
7.20	2410	2460
7.60	2390	2485
8.14	2415[1]	2485[1]
9.0		2480
9.57		2500[2]
11.0		2600[2]
11.0		2680[2]
12.0		2700[2]

[1] Average of four determinations.

[2] Determined by melting uranium in graphite crucible, holding molten for one hour at specified temperature, and furnace cooling.

The solid portion of the diagram in the range of compositions between UC and UC_2 was determined by heating samples of known composition at predetermined temperatures for nominal periods of time in vacuum and cooling by water quenching. Metallographic examination of the quenched sample then revealed whether it had been heated in a single- or two-phase region. Fig. 3 shows the microstructures of a number of compositions of uranium-carbon alloys water quenched after having been heated at various temperatures. All of the photomicrographs were originally 250×, but their dimensions were reduced about $2\frac{3}{8}$× when copied.

The samples quenched from 1700°C (Fig. 3, lower row of photomicrographs) represent the two-phase regions (see Fig. 1) consisting of U_2C_3 and either UC or UC_2. The alloy containing 4.9 weight per cent carbon shows the U_2C_3 as the grain-boundary (light-etching) phase; UC is the dark-etching predominant phase. A greater amount of U_2C_3 can be noted in the alloy containing 5.4 weight per cent carbon. The center picture in this row, showing the 6.6 weight per cent carbon alloy, is predominantly U_2C_3 with UC as the excess, dark-etching phase. In the sample containing 8.1 weight per cent carbon quenched from 1700°C, the U_2C_3 is present as the grain-boundary phase, with the principal phase being UC_2. The sample with 9.0 weight per cent carbon shows U_2C_3 as a scatter of light-colored dots, with UC_2 again the predominant phase. The presence of U_2C_3 in this sample, which is not warranted by the constitutional diagram, is probably due to the fact that this alloy contains 0.6 weight per cent free carbon in the form of graphite flakes. This leaves only about 8.4 weight per cent carbon combined with uranium. The graphite flakes appear to be inert with respect to the solid carbides and, therefore, do not affect the equilibrium reactions between these phases. This composition may well be in the region of the diagram where a slight amount of U_2C_3 can exist in equilibrium with UC_2 at 1700°C.

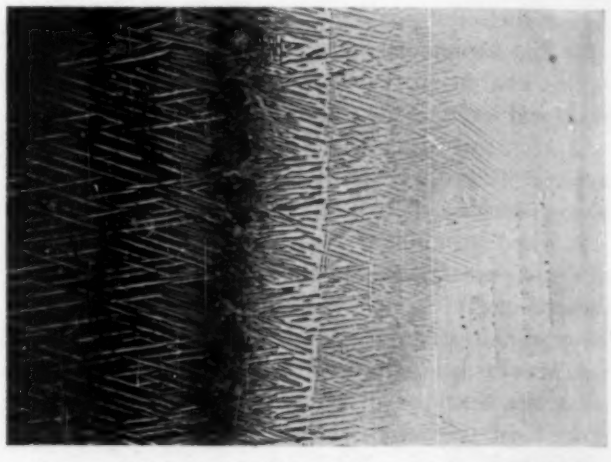

FIG. 2. Diffusion bands formed by melting uranium in a graphite crucible and furnace cooling. Right side in contact with crucible. Dark-etching phase, UC; light-etching phase, UC_2—nitric-acetic etch. 50×.

Samples containing 4.9 weight per cent carbon, quenched from 1800°C (see Fig. 3), 5.4 weight per cent carbon quenched from 1800°, 1900°, and 2000°C, and 6.6 weight per cent carbon quenched from 1800°, 1900°, and 2000°C, were all quenched from the two-phase region consisting of UC and UC_2 (refer to Fig. 1). In all of these cases, the dark-etching phase is UC, while the light-etching phase is UC_2. The microstructures of the 4.9 weight per cent carbon alloy quenched from 1900°, 2000°, and 2100°C, and the 5.4 and 6.6 weight per cent carbon alloys quenched from 2100°C indicate that these were all quenched from a one-phase solid-solution region. The

dark areas visible in the 4.9 weight per cent alloys quenched from 1900°, 2000°, and 2100°C are due to chipping out of sections of this brittle alloy during metallographic preparation. The comparatively fine precipitate of UC_2 noted in the 5.4 weight per cent alloy quenched from 2100°C is shown clearly in Fig. 4*a*. This precipitate must have formed on cooling through the UC-UC_2 two-phase region. Fig. 4*b* shows a sample of the same composition (5.4 weight per cent carbon) cooled less rapidly by furnace cooling from 2100°C. In this case, the precipitate of UC_2 is very well developed along certain crystallographic planes (Widmanstätten type) and also in the grain boundaries due to the longer time available for cooling through the two-phase region.

The microstructure of samples of uranium carbide containing 8.1 and 9.0 weight per cent carbon does not appear to change greatly with temperature of quench from 1800°C up to the melting temperature. In the alloy containing 8.1 weight per cent carbon, the microstructure in all cases consists of a finely divided but easily resolved precipitate of UC from the solid solution, as can be seen in Fig. 3. The grain size is quite large and many small grains are found along the grain boundaries of the large grains. One of these structures is more clearly shown in Fig. 5*a*. In each large grain, a series of twinning bands can be noted, a precipitate of UC from UC_2-rich solid solution being visible in each band. This suggests that, upon quenching these alloys, a reaction similar to the martensite transformation in steels may occur as a result of a shearing action within the grains which is analogous to twinning. Similar microstructures have been noted in the In-Tl system, as well as other alloy systems for which the mechanism of formation was ascribed to double shear (15). Since the reaction takes place very rapidly, it is not possible to prevent precipitation of UC from the solid

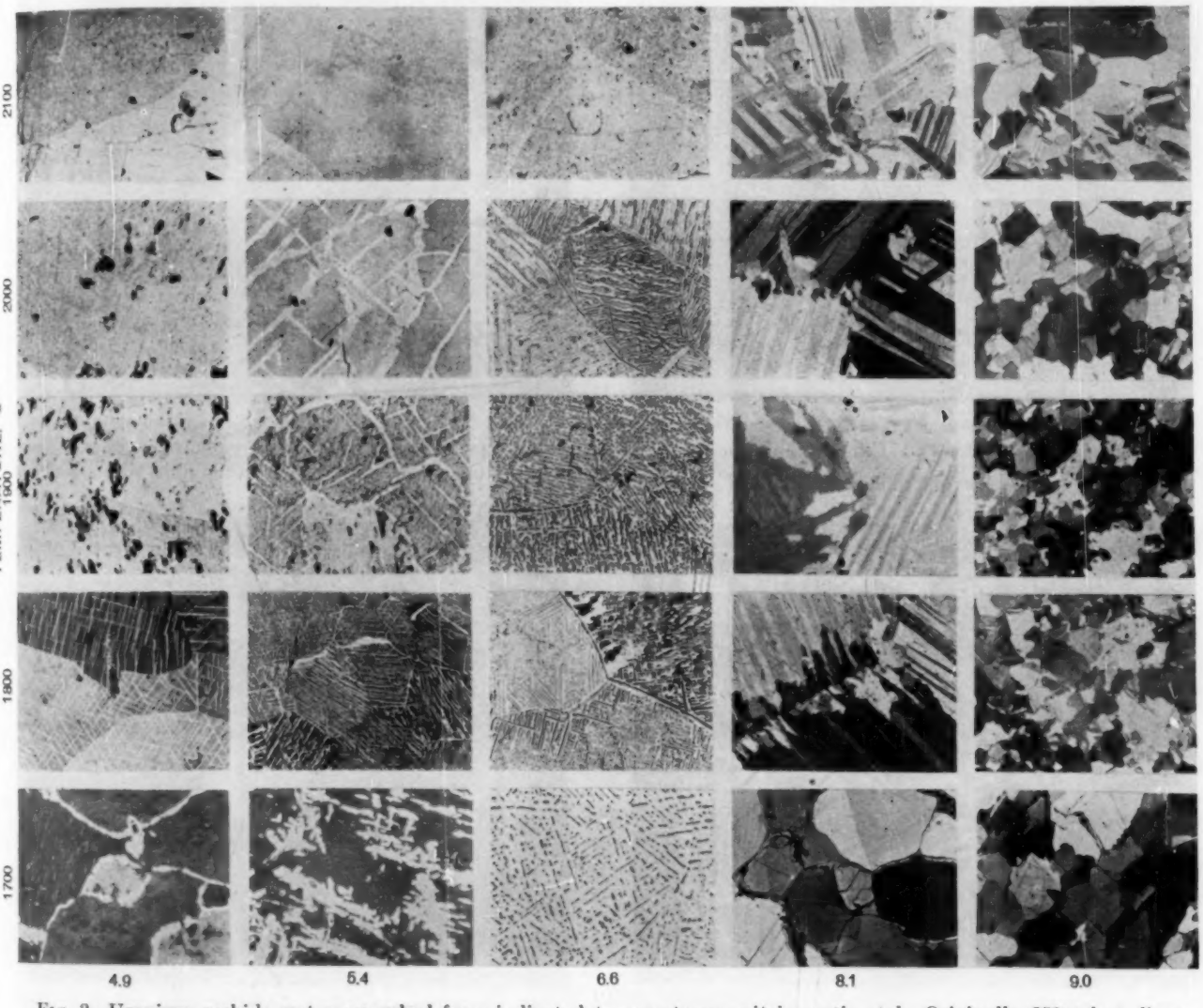

FIG. 3. Uranium carbide water quenched from indicated temperatures—nitric-acetic etch. Originally 250× but dimensions were reduced about 2⅜× when copied. (Figures below photomicrographs represent weight per cent carbon.)

solution. Cooling alloys of this carbon content less rapidly allows the precipitate of UC to develop to a greater extent, thus reducing the twinning process. Fig. 5*b* shows the 8.1 weight per cent carbon alloy furnace cooled from 1800°C. Therefore, it appears that all of these samples must have been in equilibrium in a solid-solution region between 1800°C and the melting temperature of the alloy, as is shown in Fig. 1.

FIG. 4*a*. 5.4 weight per cent carbon arc-melted alloy, water quenched from 2100°C. Dark-etching phase, UC; light-etching phase, UC_2—nitric-acetic etch. 250×.

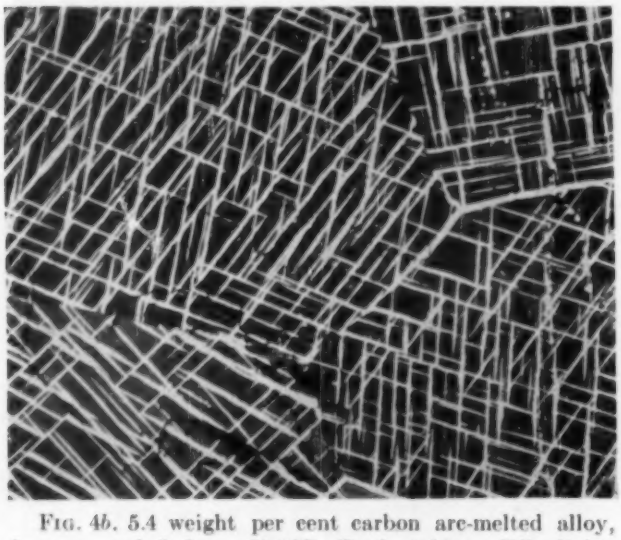

FIG. 4*b*. 5.4 weight per cent carbon arc-melted alloy, furnace cooled from 2100°C. Dark-etching, UC; light-etching, UC_2—nitric-acetic etch. 250×.

Very little change can be noted in the microstructure of samples of the ingot containing 9.0 weight per cent total carbon when quenched from temperatures above 1800°C. Fig. 6*a* shows in better detail the microstructure of this alloy when water quenched from 2100°C. Flakes of free graphite can be noted in this sample, as well as an absence of precipitated UC which is effectively retained in solid solution by quenching. The difference in shade noted among the individual grains in this photomicrograph results from black and white photomicrography of the multicolors produced by differential etching of the variously oriented grains of this sample.

The grain size noted in the microstructure of the 9.0 weight per cent carbon alloy is small compared with that of the 8.1 weight per cent carbon alloy and probably originated in cooling from the melt. Apparently the first precipitated constituent, graphite, in the 9.0 weight per cent carbon alloy furnishes numerous nuclei for the formation of UC_2 grains. Upon reheating to high temperature, the grain size remains essentially the same probably because of the inhibiting effect on grain growth of the presence of free graphite.

When the 9.0 weight per cent carbon alloy is fur-

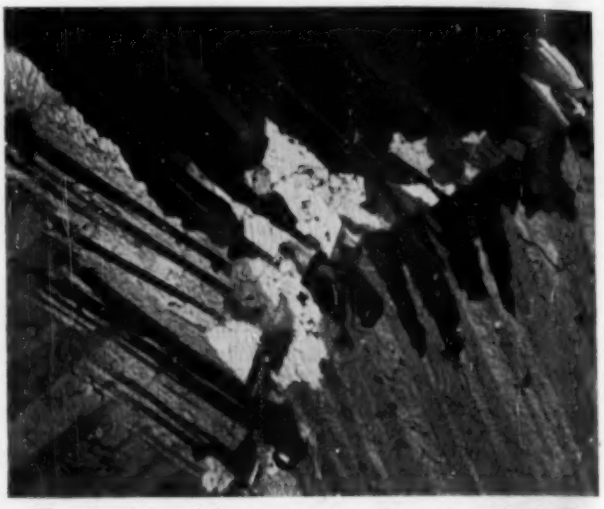

FIG. 5*a*. 8.1 weight per cent carbon arc-melted alloy, water quenched from 1800°C. Predominant phase, UC_2; precipitated phase, UC—nitric-acetic etch. 250×.

FIG. 5*b*. 8.1 weight per cent carbon arc-melted alloy, furnace cooled from 1800°C. Light-etching phase, UC_2; dark-etching phase, UC—nitric-acetic etch. 250×.

nace cooled, instead of water quenched, a lamellar precipitate of UC is formed. Fig. 6*b* shows the UC precipitate, in addition to free graphite, in the microstructure of a sample furnace cooled from 2100°C. This seems to indicate that in this alloy the precipitation of UC from solid solution takes place at temperatures below 1800°C. U_2C_3, the stable phase existing

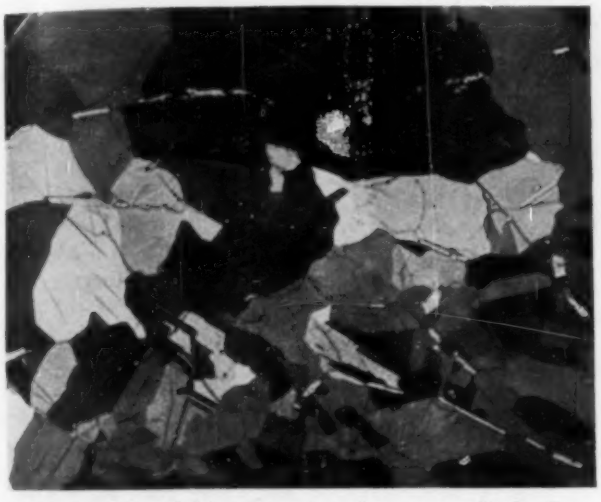

FIG. 6*a*. 9.0 weight per cent carbon arc-melted alloy, water quenched from 2100°C. Predominant phase, UC_2; gray flakes of free graphite—nitric-acetic etch. 250×.

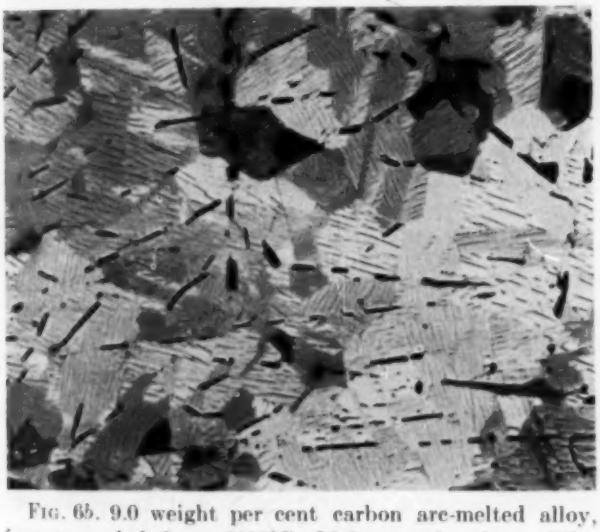

FIG. 6*b*. 9.0 weight per cent carbon arc-melted alloy, furnace cooled from 2100°C. Light matrix phase, UC_2; dark fine line lamellar precipitate, UC; dark gray-black flakes of free graphite—nitric-acetic etch. 250×.

in this region of the diagram, has never been produced on cooling through this temperature range without the addition of external energy in the form of work. A slight amount of stressing, even as little as jostling the sample about in the crucible by means of a remotely controlled tungsten rod while heating in the temperature range at which U_2C_3 forms, is sufficient to cause the transformation from UC and UC_2 to U_2C_3 to take place. This is fully described in a previous paper (8).

No additional compounds having carbon contents greater than UC_2 have been detected. It is, therefore, believed that the two-phase region consisting of UC_2 and graphite extends to the composition of pure graphite.

Discussion

Complete miscibility of UC and UC_2 at elevated temperature is a rather startling phenomenon, in view of the difference between the structures of the two phases. The monocarbide is cubic and the dicarbide tetragonal. However, other instances of solid solubility between cubic and tetragonal structure have been found (16, 17). For example, there appears to be complete miscibility between face-centered-cubic nickel and face-centered-tetragonal gamma manganese, the cubic lattice transforming with increasing manganese content, without apparent discontinuity in the x-ray patterns.

UC is face-centered-cubic, $a_0 = 4.951$ Å, of the NaCl type. UC_2 may be described on a face-centered-tetragonal cell, $a_0 = 4.96$ Å, $c_0 = 5.95$ Å, which is equivalent to the body-centered structure determined by Rundle, *et al.* (7). The uranium atoms are at the origin and face-center positions. Of the four possible positions for the carbon atoms considered by these workers, the set which places pairs of carbons along the *c*-axis between uranium atoms was selected as most likely on the basis of intensity and structure considerations. This arrangement may be thought of as a distorted *RX* (NaCl) structure with C_2 groups replacing *X* atoms.

On the basis of the similarity between the two structures, it is not difficult to conceive of a continuous transition from the monocarbide to the dicarbide structure, merely by substitution of C_2 groups for single carbon atoms. Such a substitution involves little distortion of the structure, as is evidenced by the similarity between the unit-cell size of UC and the a_0 spacing of UC_2. It would be desirable to test this hypothesis by means of x-ray diffraction examination of compositions between UC and UC_2, at temperatures above 1800°C.

An alternative possibility is a polymorphic transformation of UC_2 at elevated temperatures. This might also be checked by high-temperature x-ray studies.

In cooling from the solid-solution region, three distinct types of Widmanstätten precipitation have been noted in uranium-carbon alloys in the compositional range from UC to UC_2:

1. In alloys containing between 4.8 and about 6.5 weight per cent carbon, UC_2 precipitates from the UC-rich solid solution, because the (110) plane of the UC_2 lattice has identical spacing with the (200) plane of the UC lattice. It is understandable that, in

alloys having a UC matrix, UC_2 precipitates on the cube faces of UC (see Fig. 4*b*).

2. UC precipitates from the UC_2-rich solid solution in alloys containing between about 6.5 and 7.5 weight per cent carbon. It is assumed that, in the solid-solution field, the two lattices may be very nearly isomorphic, and again precipitation occurs on the cube faces (see central portion of Fig. 2).

3. It appears that, in alloys containing above about 7.5 weight per cent carbon, the tetragonality of the UC_2 is established and becomes more and more pronounced with increasing carbon content. From a solid solution of this structure, precipitation (of UC) occurs only on (110) planes, thus producing the lamellar-type microstructure observed in these alloys (see Fig. 5*b*).

It has not been possible to produce the dicarbide of uranium of stoichiometric composition of UC_2 with respect to the combined carbon. The maximum combined carbon found in uranium-carbon alloys by subtracting the free carbon from the total carbon reported in chemical analysis has been about 8.7 weight per cent. More often the combined carbon has ranged between 8.3 and 8.5 weight per cent. Various techniques have been tried, with little success, to increase the percentage of combined carbon.

All this would seem to indicate that the temperature horizontal, drawn at about 2480°C in Fig. 1, must extend down to a composition of at least 8.7 weight per cent carbon, leaving the UC_2 crystal lattice deficient in carbon atoms. On cooling from the liquid through this region of the diagram, solid carbon is the first constituent to be discarded from the melt. The precipitated carbon forms fairly large graphite flakes. Extended heating at temperatures below the solidus is not sufficient to put it into solution again.

Acknowledgment

The authors wish gratefully to acknowledge the following valued aid from other members of Battelle Memorial Institute staff: the melting of many of the master alloys and ingots under the direction of J. G. Kura and M. C. Udy; x-ray studies by C. M. Schwartz and D. A. Vaughan; chemical analysis carried out by Battelle analytical group under the direction of E. J. Center; and the counsel of G. K. Manning and H. A. Saller on various phases of the metallographic work.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the JOURNAL.

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A Technique for Eliminating Crucibles in Heating and Melting of Metals[1]

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ABSTRACT

An original method of heating and melting metals without a crucible, by suspension in space with an electromagnetic field, is described. The required field was generated by applying high frequency alternating current to two coaxial coils connected in series opposition. Stable levitation and heating of various metals in the solid state was obtained between the coils in the vicinity of the common axis, both in air and in a vacuum. Weights levitated ranged up to 550 grams. In air, some tens of grams of Al, Sn, and a brass were brought to melting and continued in levitation while in the liquid state. In a vacuum, 10 grams of Al was successfully levitated molten. On the other hand, several attempts to levitate molten Ag, Ti, and Zr in a vacuum failed.

Method of Attack

In melting the more reactive high-melting point metals such as titanium, zirconium, vanadium, tantalum, molybdenum, and others of similar chemical and physical characteristics, difficulty is usually encountered due to reaction with crucibles. Other reactions occur which adversely affect the quality of the melt. For example, titanium, when melted in a graphite crucible, will contain several tenths to one or more per cent of carbon. When zirconium is melted in contact with oxide type crucibles, it becomes embrittled because of absorption of oxygen from the refractory. If the crucible is sufficiently cooled, in an effort to reduce contamination of the melt, then other unsatisfactory results may appear. When melting metals in a crucible of water-cooled copper, as in the arc-melting process, the ingot has a very rough surface and often possesses holes or voids.

In view of the prevailing difficulties, a technique which would reduce or prevent contamination, and provide continuous agitation of the melt is required. In an attempt to realize this objective, several plausible methods were considered. Of these methods, the most promising was the use of alternating magnetic fields.

Initial experiments, in air, involved a single solenoid mounted with its axis vertical. Although a brass specimen was supported by the alternating magnetic field established by the energized coil, it drifted laterally from the coil axis and fell out of the influence of the field. With more power the levitated specimen rotated, melted, and thereupon uncontrollably flowed down out of the influence of the coil field. The experiment was repeated with other metals with the same undesired results. However, these initial experiments with brass, tin, and aluminum specimens up to 550 grams indicated that in the solid state at least, vertical support by an alternating magnetic field was possible. It remained to investigate the magnetic field distribution required for stable levitation of molten as well as solid metals, including controlled draining of the melt (1).

It was discovered that one way in which an adequate radial restoring force would be realized was by two coaxial coils, as illustrated in principle by Fig. 1. They are connected in series across a common capacitor so as to constitute a parallel tuned load to the alternator. The currents in these fixed coils induce in the interposed metal charge, which may for example be a sphere as in Fig. 1, eddy currents whose interaction with the inducing field gives rise to the necessary supporting and lateral restoring forces. These make possible stable levitation of solid metal specimens, and are at least the principal factor in floating the subsequently molten metal when that can be done. Heating of the levitated specimen depends upon the power available, coupling between primary circuit and specimen, frequency, eddy current and hysteresis losses in the specimen, and heat losses from the specimen. When the metal can be melted while levitated, it assumes the shape of a top as illustrated presently; vigorous stirring occurs; and there is a tendency to rotate, which, however, can be suppressed by introducing some axial asymmetry.

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Initially, difficulty was experienced in preventing molten metal from draining from the bottom. This was overcome by modification of the coil form, so that finally molten levitated metal could be wholly prevented from draining, or drained slowly, or drained suddenly, by merely adjusting the current properly.

Everything that has been said thus far in this section refers to a first phase of the investigation, which took place at Bloomfield. The Bloomfield ideas and findings were communicated to East Pittsburgh, where a second phase was then undertaken. In this second phase, experiments were made in a vacuum as well as in air.

When metals were floated liquid in air, e.g., aluminum, it was evident that they soon became coated with oxides or other compounds. How important was this oxide coat in making liquid levitation possible?

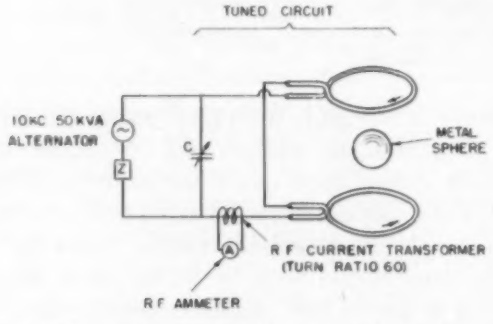

FIG. 1. Schematic circuit diagram of levitation experiment.

On the one hand, it seemed it could not be of much account, for the vigorous agitation of molten metal cracked whatever film was formed, so that islands of film swam on the surface. On the other hand, stability of a melt with coils of the type in Fig. 1 might depend on preventing pour from starting at the bottom up. A film of oxide just there might possess an efficacy out of proportion to the area it covered. Since the chief applications of the method would of course be in a vacuum or a protective atmosphere, where little or no film would form, the East Pittsburgh trials were of major interest.

Coils employed at East Pittsburgh were similar to some of those at Bloomfield, to be described in the following section. Currents ranged up to about 1200 amp. Frequency was always 9600 cycles at East Pittsburgh, 10,000 cycles at Bloomfield.

In air, in the solid state, various masses of aluminum, silver, and aluminum bronze were floated stably just as at Bloomfield. In air again in the liquid state, aluminum was floated with ease. Molten silver was supported between coaxial coils on one occasion, but drifted laterally out of the field. On other occasions, when melting commenced, the liquid silver drained downward and dripped away from the lower surface of the remaining solid metal, apparently without much interference from the alternating field which was concurrently supporting the solid metal. It is to be observed that silver melts in air without forming a protective oxide film like aluminum.

In a vacuum of 10^{-4} or 10^{-5} mm of Hg, there was no difficulty in levitating aluminum, silver, and titanium in the solid state. On melting, however, aluminum usually dripped downward, even in a coil and with a current that would have supported the liquid if surrounded by air instead of vacuum. Proposed solutions are discussed in a subsequent paragraph. In the end it was found possible to levitate approximately 10 grams of molten aluminum in vacuo for about one minute. But even then it became apparent that there was still a film which segregated as wrinkles at preferred sites on the molten surface.

A lump of titanium was almost completely melted while in levitation. Silver, however, always began to drain as soon as it melted. At the same time opaque films began to form on the inside surface of the bell jar which enclosed the vacuum, so that observation of melted silver could never be carried on long.

In another approach to the problem, a pair of parallel conductors were employed instead of coils. The conductors were 6-in. lengths of $\frac{3}{8}$ in. OD copper tubing, with a 1-in. space between. Currents, in phase conjunction, reached about 2000 amp. Bars of aluminum, zirconium, and copper, about $\frac{1}{2}$ in. in diameter and 4 in. long, were readily floated in the solid state between the conductors. In hydrogen atmosphere to eliminate oxide coating, a copper bar was floated partially molten. Support of completely molten metal was not achieved by this arrangement, however.

EXPERIMENTAL WORK

At Bloomfield, slugs of any shape of various conductive materials could be levitated in the space between the coils, as illustrated by Fig. 2. Brass, Al, Sn, compacted Ti powder, Mo, and others were used in the experiments. The solid specimen was levitated by increasing the alternating current in the coils as illustrated by Fig. 2*b*. The levitated specimen began to heat, and the rate of its temperature rise could be controlled by varying the magnitude of the alternating current. In those cases in which the specimen continued to be supported while melted, it assumed the shape of a top as illustrated by Fig. 2*c*. In several experiments molten aluminum was introduced into the interaction space; it immediately assumed the form illustrated by Fig. 2*c*. In the levitated state the molten mass was vigorously agi-

tated by the alternating magnetic fields. The specimen tended to rotate about the axis of symmetry, but this could be prevented as already mentioned. The molten levitated mass could be drained into a suitable receptacle, as illustrated by Fig. 2*d*, or dropped as a whole, by merely adjusting the current in the coils. It may even prove possible to resolidify the levitated molten metal, perhaps with the aid of gas blast cooling (in the case of melting in a protective atmosphere) or by control of the temperature of the surroundings.

In an effort to obtain preliminary design data so as to provide more effective and stable levitation of the molten metal, many types of coil systems were

FIG. 2*a* FIG. 2*b*

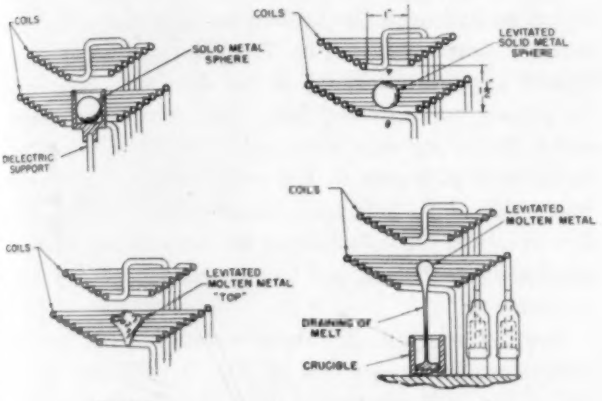

FIG. 2*c* FIG. 2*d*

FIG. 2*a*. Insertion of the solid metal sphere into the coaxial conical coil system.

FIG. 2*b*. Heating and levitation of the solid metal sphere by the coaxial conical coil system, connected series opposition.

FIG. 2*c*. Melting and agitation of the molten metal "top" by the coaxial conical coil system.

FIG. 2*d*. Controlled draining of the levitated molten metal by the coaxial conical coil system.

investigated. Some are illustrated by Fig. 3–5. In all these four figures the approximate shape of the molten levitated metal is shown. It is inherent in the coil designs of Fig. 1–5 that the minimum levitation force exists at the coil axis. This results in the tendency to drip. Two schemes may be employed to alleviate this. The first would be to create the field with current sheets or with a coil oriented as in Fig. 10. The second solution may be to move the minimum in such a manner that the inertia of the molten metal prevents dripping.

The latter may be accomplished by mechanically or electrically rotating magnetic fields. Single and polyphase systems appear feasible. Experimentally only the single phase system of Fig. 6 was tested. The molten levitated metal assumed an approximately spheroidal form. Even though the desired results are produced by this scheme the complication of the coil system is a serious disadvantage. Electrical rotation of the alternating magnetic field for levitation of the molten specimen is preferred over mechanical, but the latter may have some advantages in the simplicity of the coil system.

Fig. 7*a* and 7*b* illustrate the coil system of Fig. 5 and the method of introducing the metal sphere by means of a dielectric tube into the interaction space. Fig. 7*c* illustrates the withdrawal of the dielectric tube and levitation of the metal sphere in the inter-

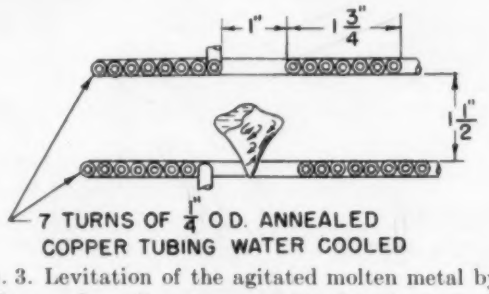

FIG. 3. Levitation of the agitated molten metal by the coaxial pancake coil system connected series opposition.

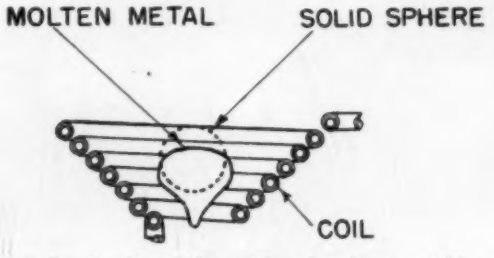

FIG. 4. Levitation of the solid and molten metal by single conical coil.

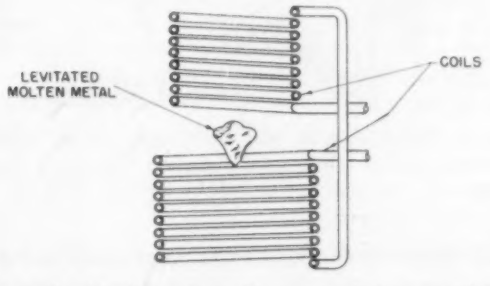

FIG. 5. Levitation of molten metal by coaxial coil system, connected series opposition.

action space by the induction fields of the two coils connected in series opposition. The meter indicates a circulating current of 600 amp in the coils when connected as illustrated schematically by Fig. 1. Appreciable restoring forces were experienced when the metal sphere was pushed in various directions from its equilibrium position in the interaction space. Fig. 8*a* and 8*b* illustrate the sideward and downward pushing of the metal sphere by a glass tube. In each case the sphere returns to its equilibrium position near the center of the coil system as illustrated by Fig. 7*c*, when the glass tube is removed.

The aluminum specimen was allowed to start melting in air while levitated by the alternating magnetic field of the coils. As it did so it assumed the shape of a top as illustrated by Fig. 7*d*. As melting of the levitated specimen progressed, portions thereof flowed downward and periodically dropped out of the field. In order to avoid this tendency to draining, the size and mass of the levitated metal may be decreased, or the circulating current in the coils may be increased, or the coils may be more effectively shaped in order to levitate both the molten and solid

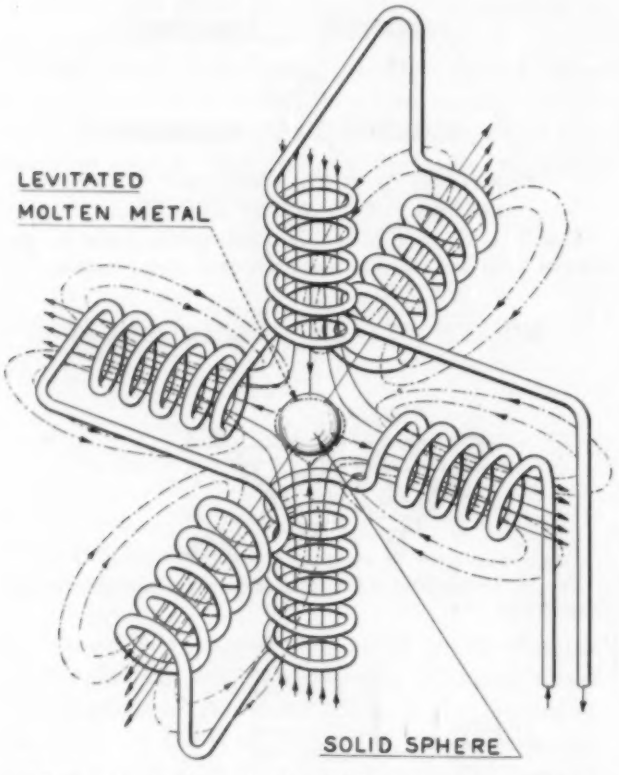

FIG. 6. Levitation of the solid and molten metal by multi-coil system with more complex field than those of Fig. 1–5.

metal. All of these expedients were tried and found to stop drainage.

Fig. 7*c*, 7*d*, 8*a*, 8*b* illustrate an aluminum specimen which was not only readily levitated and melted by the indicated current of 600 amp, but could be drained under control by reducing the circulating current in the coils to 540 amp, as illustrated by Fig. 7*e*. The thin column shown projecting from the bottom of the coil is molten metal draining from the molten levitated portion seen between the coils.

Experiment indicates that for most effective levitation and induction heating of a metal specimen an optimum coil configuration exists, and that it varies with the type of specimen and whether it is in molten or solid state. Although data have been obtained regarding the levitation characteristics of various coil configurations, it is only in a preliminary stage and not sufficiently established for general application. However, it is appropriate to cite a few typical experiments. One such experiment involves a double pancake coil system as illustrated essentially by Fig. 3. The circulating coil current was about 480 amp. About 9 kw was supplied to the tuned circuit (most of this power was lost in this circuit). An aluminum sphere approximately 1 in. in diameter, weighing 21.5 grams, was inserted into the interaction space between the coils. The specimen on melting assumed the form illustrated by Fig. 3 and remained stably levitated for as long as desired. Severe turbulence was noticed, but no spinning occurred. When the circulating coil current was reduced to 312 amp the molten metal drained in the manner portrayed in Fig. 7*e*. When an aluminum sphere approximately 1½ in. in diameter, weighing 70 grams, was inserted into the interaction space, stable levitation was obtained for solid and molten metal with 570 amp in the coils. When the current was reduced to 360 amp about half of the metal flowed out of the influence of the field in the manner previously described, and the remainder fell onto the bottom coil.

Another example involves a double coil system combining the upper coil of Fig. 3 with the lower coil of Fig. 2. Some results were as follows:

Specimen	Circulating coil current	Comments
Al sphere, 1 in. diam, 21.5 g	630 amp	Improved stability of levitation of both solid and molten metal as compared with double pancake coil system of Fig. 3.
Mo sphere, 154 g	720 amp	Stable levitation of the solid up to red heat was observed. No attempt was made to go higher.
Ti cylinder ½ in. diam, ⅝ in. long, 13 g	720 amp	At the threshold of levitation of the solid. Specimen heated very quickly. No attempt was made to melt.
Cu sphere, 80 g	630 amp	Excellent levitation of the solid. Specimen heated to 480°C. No attempt was made to melt.
Brass cylinder, ¾ in. diam, ¾ in. long, 50 g	492 amp	Satisfactory levitation of the solid.

In this same coil system it was possible to feed a ⅛-in. diameter, 1-in. long aluminum rod into the molten metal from above without disturbing its stability.

As a final example, a double conical coil system illustrated by Fig. 2 was tested. The coils were con-

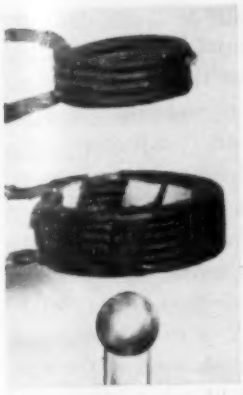

FIG. 7a

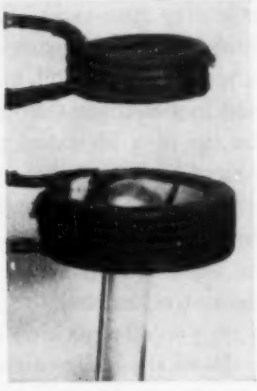

FIG. 7b

FIG. 7c

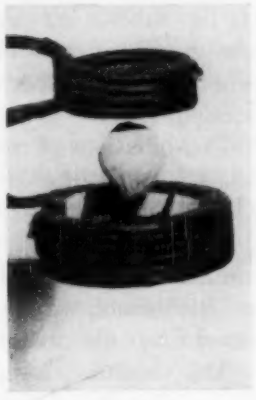

FIG. 7d

FIG. 7a. Solid metal sphere resting on glass tube and ready to be inserted into the interaction space of the coil system of Fig. 5.

FIG. 7b. Insertion of the solid metal sphere into the interaction space

FIG. 7c. Levitation of the solid metal sphere. Glass supporting tube withdrawn

FIG. 7d. Levitation of the molten metal

FIG. 7e. Draining of the levitated molten metal

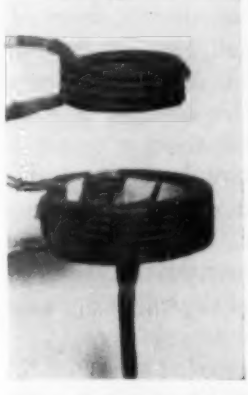

FIG. 7e

nected in series opposition. Some results obtained for an aluminum sphere 1 in. in diameter were as follows:

θ	ψ	Circulating coil current	Input power to tuned circuit	Comments
75°	75°	552 amp	9.8 kw	Levitation of the molten metal is inadequate and so it drains out of the field.
90°	90°	492 amp	8.2 kw	This condition represents a threshold of levitation of the molten metal. The metal drains out of field on slight disturbance.
90°	90°	600 amp		Improved levitation of molten metal.
120°	120°	426 amp	8.1 kw	Stable levitation of molten metal.
120°	120°	600 amp		Excellent stability.
120°	180°	426 amp	8.1 kw	Excellent stability.
120°	180°	600 amp		Excellent stability.

Fig. 9 illustrates the levitated molten aluminum in the interaction space. Solid metal spheres seem not to be effectively levitated by double coaxial coils of the type illustrated by Fig. 2 when the coil angles $\theta = \psi = 75°$ approximately. For $\theta = \psi \geqq 120°$ the coil system provides an interaction field

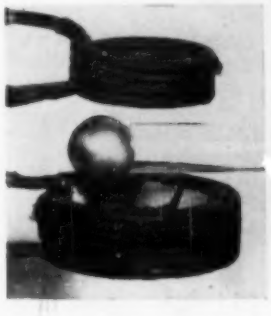

FIG. 8a

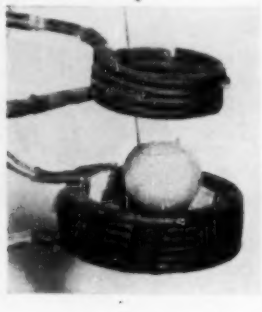

FIG. 8b

FIG. 8a. Pushing the solid metal sphere sideways in the interaction space by the glass tube to illustrate the strong restoring forces acting on the sphere.

FIG. 8b. Pushing the solid metal sphere downward in the interaction space by the glass tube to illustrate the strong restoring forces acting on the sphere.

well suited for effective levitation of the molten metal.

These preliminary evaluations are subject to some criticism in that several relevant factors are not readily controlled.

Some attention was paid to levitation of solid spheres in solenoids. Aluminum spheres 1 in. in diameter were successfully levitated at the center of a solenoid as illustrated by Fig. 10. The lateral stability was satisfactory and tendency to drainage of the melt was negligible. Better stability may be obtained at the axial vertex of an arc-shaped solenoid, Fig. 10, than at the center of the usual straight solenoid. These coil configurations may prove on further investigation as satisfactory as, if not superior to, the other arrangements cited in this report.

What precedes in this section refers to the work

at Bloomfield. We now add a few details regarding the experiments at East Pittsburgh, the nature of which was described at the end of the previous section.

Combinations of coils similar in shape and dimensions to those shown in Fig. 2–4 were tested. The OD of the copper tubing was usually $\frac{5}{16}$ instead of $\frac{1}{4}$ in. As already mentioned, experience in air with aluminum, both solid and molten, paralleled that at Bloomfield, while efforts at supporting molten silver in air met with little success.

The vacuum trials were made under a bell jar of $9\frac{1}{2}$ in. ID and 18 in. inside height. This was mounted

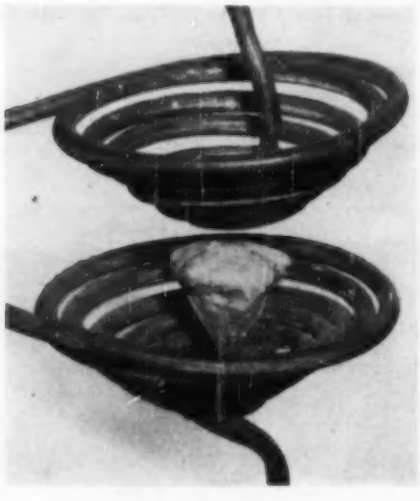

FIG. 9. Levitation of the molten metal by the coil system of Fig. 2.

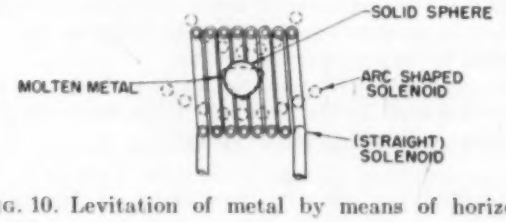

FIG. 10. Levitation of metal by means of horizontal solenoid.

upon a vacuum system consisting essentially of a few feet of 8-in. Monel pipe. Closures were rubber gasketed. The system was evacuated by a Westinghouse 8-in. oil diffusion pump backed by a Distillation Products 8-in. MB-300 booster pump and a Kinney CVD8610 mechanical pump. Pressures during levitation runs were in the range 10^{-4} to 10^{-5} mm of Hg as measured by a Radio Corporation of America type EMG-1 cold cathode discharge vacuum gauge.

The metal to be levitated was at first laid in an alumina cone that nested into the lower coil. Later, the charge was initially supported on a water-cooled pedestal of either nonmagnetic (molybdenum) or magnetic metal (Hipernik, a Westinghouse high permeability iron-nickel alloy). It was hoped that the pedestal, which reached up into the bottom-most turn of the lower coil, might alter the electromagnetic field in a manner favorable to preventing pour from the tip of a levitated melt. Other expedients that seemed to improve stability at different times were: (*a*) brazing a $\frac{1}{8}$-in. thick copper ring of 1 in. OD and $\frac{1}{4}$ in. ID, split in the manner of a lock washer, within the bottom-most turn of the lower coil so as, in effect, to diminish the radius of that turn; and (*b*) setting copper plates $\frac{1}{4}$-in. thick in such positions as to shield the space within the coils against the stray fields due to the currents in the leads to the coils.

In vacuo, as in air, it was possible to levitate and heat various metals in the solid state, and to levitate aluminum in the liquid state as already described. For example, an aluminum ball 1 in. in diameter was floated by means of currents of 600 to 800 amp. It split in half, but one half continued to float, melted, then floated molten for about a minute in the shape of a thin pear with point down. The surface appeared very bright and clean at first, but toward the end traces of film were seen. The gauge indicated a vacuum of 10^{-5} mm throughout the run. This success followed the introduction of the split copper ring mentioned above.

The parallel conductors described at the end of the preceding section each spanned a short gap in a copper ring of approximately 18 in. OD, 14 in. ID, and 2 in. axial dimension. Several turns of insulated $\frac{3}{8}$ in. copper tubing, wound as a "pancake" coil of the same OD and ID as the copper rings and clamped between the rings, served as the primary of a 9600-cycle transformer, the two rings constituting single-turn secondaries. This arrangement made possible currents of about 2000 amp in the rings and the parallel conductors.

Concluding Remarks

Although the experiments have dealt with masses of the order of a few hundred grams, and circulating currents of the order of 700 amp at about 10,000 cycles per second, these magnitudes do not necessarily represent limiting or optimum values. The mass to be levitated governs, at a given frequency and coupling, the magnitude of the circulating current required, the availability of which is in turn dependent in part upon the efficiency of the coil system and tuned circuit as a whole.

Both the levitation force and the induction heating power input vary as the square of the circulating current in the coil system. Hence it is obvious that the resistance of the coil system should be a minimum. It can be shown that the frequency and the equivalent Q of the levitated mass should be such that the skin effect is appreciable. On this basis it

has been estimated that metallic masses up to several pounds may be stably levitated with a 50 kva, 10,000-cycle alternator.

If float melting can be made adaptable on a larger scale, the following advantages can be anticipated:

1. The charge touches no crucible or container during the heating, melting, and draining stages.
2. The heated or molten charge can be protected by a suitable atmosphere or a vacuum.
3. Volatile impurities can be distilled or pumped away.
4. The molten charge can be drained gradually or dropped as a whole, and it may even be feasible to solidify the still levitated melt and then drop it solid.
5. The melt is thoroughly mixed electromagnetically.
6. The charge can consist of metal powders and alloying constituents mixed and sintered together or bound by a suitable binder.
7. Alloying additions can be made while the melt is in levitation.

A limitation of the existing coil systems is the relatively low electrical heating efficiency of induction coils surrounding a relatively small charge.

It cannot be said that the feasibility of levitating molten metal in a protective atmosphere or in vacuo has been firmly established. The nearest approaches were the experience in a coil in vacuo with the aluminum ball that split, and between parallel conductors in hydrogen with the copper bar that partly melted. It seems certain that oxide coats which form in air make float melting easier, but whether such coats are essential, at least for charges beyond a certain size, remains to be investigated further.

Acknowledgment

We wish to take this occasion to acknowledge our obligations to those who aided us in realizing a measure of our object. Our appreciation is due to E. G. F. Arnott, Director of Research at Bloomfield, for encouragement and assistance, to E. Gregory and J. G. Jacobsen for contributions to the experimental work, and to L. F. Ehrke and W. Adamus for photography. We are most grateful for the contributions at East Pittsburgh of J. A. Hutcheson, Vice-President, C. M. Slack, the late R. C. Mason, and of L. S. Castleman, J. W. Salatka, and C. R. Simcoe.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1952 issue of the Journal.

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Some Factors in Anodic Processes on Corroding Metals[1]

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ABSTRACT

Many alloying elements that confer resistance to high-temperature oxidation also prevent low-temperature aqueous corrosion; they produce oxide films that only slowly transmit cations. Conversely sulfur, which introduces lattice defects into the films and thus favors the transmission, accelerates high-temperature oxidation and favors the onset of aqueous corrosion. It is therefore suggested that the onset of aqueous corrosion is controlled by the relative ease with which cations can pass through the original air-formed oxide film on the metal. A rapid supply of dissolved oxygen to all parts of the surface may arrest cations as they emerge, thus thickening the film and preventing corrosion; a far more rapid supply of oxygen is needed to prevent corrosion on iron or zinc than on stainless steel, but the supply needed is diminished if an inhibitor is present. The weakest places in the film are those where cations can most readily pass through; they become the initial corrosion anodes. The further development of the anodic zones depends on the production of anodic acidity.

Introduction

It is established—alike by gravimetric (1, 2), optical (3), and electrometric (4, 5) methods—that a metallic surface, exposed to moist or dry air or oxygen at ordinary temperatures, becomes superficially oxidized. The oxide, which is invisible, does not, in general, protect the metal against corrosion if subsequently the surface becomes wetted with a salt solution or a natural water. On some materials, however, the superficial oxide does furnish considerable protection; these materials include alloys containing chromium and aluminum—two elements commonly added to metals to diminish high-temperature oxidation. If this is not a coincidence, it would seem that the mechanism whereby the metal begins to pass out through the invisible film into the liquid is the same as that which produces thickening of an oxide scale at high temperatures; this latter is widely believed to be an outward movement of metal.

As pictured by Wagner (6), high-temperature oxidation consists of the passage of metallic cations accompanied by electrons outward by lattice diffusion through the film[2]. The oxygen atoms already present, adsorbed on the outer surface (this will be the case if the atmosphere contains oxygen), are converted by the electrons into oxygen ions, and the cations, taking up their appropriate places between them, build up an extra lattice layer of oxide. Thus the oxide film steadily thickens by continual accretion on its *outer* surface. Wagner developed equations expressing the constant (k) of the parabolic growth-equation ($dy/dt = k/y$, where y is the thickness at time t) in terms of the electrical properties of the oxide film and the free energy of formation of the oxide. In the only three cases of combination between metal and nonmetal, where the values of these electrical properties are quantitatively known, there is good agreement (10) between the observed and calculated values of k. Further evidence for the essential correctness of the lattice-diffusion mechanism is provided by the work of Price and Thomas (11) on copper-aluminum alloys; here a preliminary heating in a *very weakly oxidizing* atmosphere produces an invisible film of alumina free from copper, and this enormously increases the resistance to oxidation exhibited when subsequently the alloy is heated in oxygen. The absence of foreign atoms in pure alumina insures an almost complete absence of lattice defects capable of allowing the outward transmission of cations and/or electrons. The improvement obtained by this preliminary selective oxidation agrees well with that predicted by the Wagner equation.

The main object of the present paper is to show that this picture of cations moving outward through a film (uncracked in the ordinary sense of the word), which has been so useful in interpreting high-temperature oxidation, can be advantageously applied in explaining and coordinating some of the known facts of wet corrosion, inhibition, and passivity.

The Two Oxidation Mechanisms

It should first be made clear that the cation diffusion mechanism, which is all-important in high-temperature oxidation and which (as suggested later) can operate *locally* at low temperatures, is by no means entirely responsible for the oxidation that

[1] Manuscript received February 1, 1951. This paper prepared for delivery before the Washington Meeting, April 8 to 12, 1951.

[2] Slightly different forms of the theory are presented by Hoar and Price (7), by Mott (8), and by Valensi (9).

proceeds when metals are exposed to (fairly) dry air at room temperature. Vernon's curves (12) for the relation between log Q (where Q is the oxidation produced on iron in a given time) and $1/T$ (where T is the absolute temperature) show two straight lines cutting at 200°C (the change-point may vary with different varieties of iron). This suggests that cation diffusion in the film—although predominant at high temperatures—becomes, below 200°C, less effective than an alternative mechanism of lower activation energy. The nature of this alternative mechanism, which is believed to be responsible for a mixed zone of interlocked oxide and metal (13), has been discussed elsewhere (14, 15); it seems to involve inward diffusion of oxygen in shattered metal to form "subscale." Presumably cation diffusion can continue even at room temperatures, but extrapolation suggests that it must account for much less than 1 per cent of the oxidation of the whole surface. At exceptional "weak spots," however, it can still be very important, as suggested below; weak spots may occur at places where the film is in tension, or where it is rich in defects or exceptionally thin, as may happen just after a true crack has developed and oxide is being rebuilt on metal that has been momentarily bare.

Outward Movement of Cations at Low Temperatures

Although low-temperature oxidation is partly *internal*, an external film undoubtedly exists, and at weak spots a relatively rapid outward passage of cations remains possible. However, where the metal is exposed to (nearly) dry air, the cations arriving at the outer surface build up extra layers of oxide and the weak points automatically heal themselves. The same occurs if the metal is placed in pure water containing dissolved oxygen—*provided that the oxygen is replenished sufficiently quickly*. Early work by one of us (16) showed that pure iron whirled in distilled water containing oxygen remained bright and unchanged (apart from occasional pin-points of rust on some specimens); the same iron in the same water under stagnant conditions rusted readily. Lately, Davies (17) has made similar observations on zinc. Presumably, the rate of supply of oxygen to the weakest point must be sufficient to "arrest" all the outward migrating cations, and retain them on the surface as fresh oxide layers instead of allowing them to enter the liquid. The rate of oxygen replenishment required depends on the rate at which cations can pass outward through the film. Alloys containing chromium or aluminum, which build films permitting only a slow outward passage of cations even where the thickness is small, suffer relatively slow oxidation at high temperatures, and require only a small rate of supply of oxygen to remain unaffected by water. There is no need to whirl aluminum or stainless steel in order to avoid attack by most waters and many salt solutions. Nevertheless, if the oxygen supply is inadequate, the corrosion of aluminum may increase; examples are provided by Bryan (18) and Ravald (19). There are many examples from industry where the removal of the last trace of oxygen from some liquid that otherwise causes no action on stainless steel has led to violent attack; interesting cases are described by Pratt (20) and Keating (21). On the other hand, iron and zinc are appreciably attacked

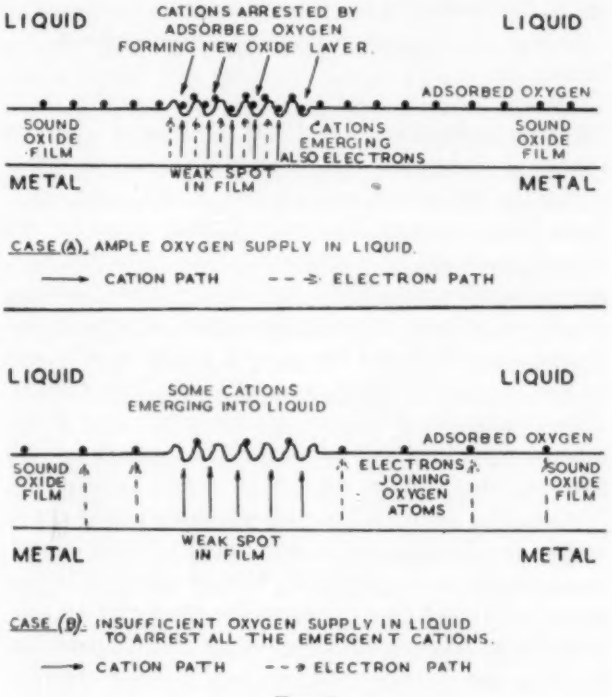

Fig. 1

by water containing oxygen unless the conditions are such as to replenish oxygen rapidly at the weakest point, since here the rate of outward passage of the cations is likely to be fast. The whirling experiments have already been mentioned, but a considerable degree of passivity has been attained on iron without whirling by Bengough and Wormwell (22) through the use of high oxygen pressures; even in the presence of chlorides corrosion can sometimes be avoided under conditions of rapid relative motion, as shown by Wormwell and Ison (23).

The difference between the two cases where the oxygen supply is adequate and inadequate is suggested in Fig. 1. In case (A), the cations are arrested and form a new oxide layer; in case (B) they emerge into the liquid. If this occurred alone, it would leave the metal negatively charged; but if oxygen is present at the parts of the film around the weak spot, electrical neutrality is preserved by electrons passing

through the film at these other parts and converting oxygen atoms into ions, which pass into solution not as O^{--} but its hydrated equivalent OH^-. Thus we arrive at the familiar mechanism of electrochemical corrosion. Metal (say, zinc) passes into the liquid as (hydrated) ions, crossing the film at its weakest spots; this (anodic) reaction can be written

$$Zn = Zn^{++} + 2e.$$

Meanwhile, oxygen is reduced to hydroxyl by the cathodic reaction, which can be written

$$O_2 + 2H_2O + 4e = 4OH^-$$

or, in two stages,

$$O_2 + 2H_2O + 2e = H_2O_2 + 2OH^-$$
$$H_2O_2 + 2e = 2OH^-.$$

Metallic hydroxides ("rust" in the case of iron) are obtained where the OH^- and the cations meet[3].

For the present purpose, however, the exact equations do not matter. The point is that metal cations passing outward, at a spot where the supply of oxygen is insufficiently rapid to "arrest" them (forming oxide), may pass on into the liquid, becoming hydrated, provided that the oxygen supply is sufficient at the (normally larger) area of sound film around. This constitutes corrosion. It can occur even if the rate of replenishment of oxygen is uniform at all parts of the surface; but it is clearly favored by "differential aeration" conditions, where the oxygen supply to a limited area is very small while at a large area nearby it is plentiful. Furthermore (25) the presence of a salt that increases the conductivity, and thus allows more distant regions to contribute effectively to the cathodic reaction, will increase the rate of movement of cations through the film. This must enhance the probability that corrosion will start at a weak point, provided that the anion introduced is one that allows the cations to enter the solution. Sodium chloride favors corrosion, since the chlorides of most metals are freely soluble; sodium phosphate is more likely to prevent corrosion, since the phosphates of most metals are sparingly soluble.

The weak point in the film may be a place where the metal had been in a state of internal stress. Internal stresses in the metal may be inherited by the oxide, as suggested by film-transfer experiments (26), although this is more likely to be true when oxygen penetrates inward than when films are formed by cation diffusion. Natural corrosion frequently starts at blemishes on an otherwise smooth surface—notably in the case of aluminum. Presumably a preliminary exposure to conditions where oxygen is present in sufficient quantity to insure that energy-rich groups of atoms are used up in producing oxide diminishes the chance of corrosion of the more destructive type setting in later. Thus copper, which when freshly abraded is everywhere blackened by silver nitrate solution, develops only isolated crystals of silver if exposed to air for some days before immersion (27). Another example of the same principle is afforded by Vernon's work (28) on iron exposed to dusty air.

Inhibitors

The arguments developed above for the mechanism of the initiation of electrochemical corrosion of metal presuppose that the metal can enter the solution as hydrated cations—which is usually the case when the salt of the metal with the principal anion present is freely soluble and not seriously hydrolyzed at the *p*H of the solution. If the anion is one which produces a sparingly soluble compound with the metal, inhibition may generally be expected, although it would be wrong to suggest that only substances having such anions can act as inhibitors.

The most effective inhibitors of corrosion are likely to be substances that make it practically impossible for cations to enter the aqueous phase at all. The rate of supply of oxygen needed to prevent corrosion on steel is smaller in the presence of such an inhibitor than in its absence, just as the rate of supply of oxygen needed to prevent corrosion on stainless steel is smaller than that needed to prevent it on iron or zinc. Recent work suggests that the function of such substances may be to enable oxygen to inhibit more effectively. Thus Pryor and Cohen (29) have shown that, whereas sodium phosphate in the absence of oxygen merely slows down corrosion, the same amount under the same conditions may stop it altogether in the presence of oxygen. Another possible explanation is that in the presence of oxygen ferric phosphate is formed instead of ferrous phosphate.

Hydroxyl ion, a typical inhibitive anion (since the hydroxides of most heavy metals are sparingly soluble), may cause oxygen to act as an inhibitor where otherwise it would accelerate attack (doubtless by promoting the cathodic reaction). Groesbeck and Waldron (30) studied the effect of oxygen concentration on corrosion by water containing sodium hydroxide and carbon dioxide in amounts adjusted to give different *p*H values. At *p*H 6.0, the corrosion

[3] In acid liquids, it is probably better to regard the cathodic reaction, not as the production of OH^-, but as the destruction of H^+

$$O_2 + 4H^+ + 4e = 2H_2O$$

or in two stages

$$O_2 + 2H^+ + 2e = H_2O_2$$
$$H_2O_2 + 2H^+ + 2e = 2H_2O.$$

The cathodic reduction of oxygen to hydrogen peroxide has been studied by Delahay (24).

velocity increased with oxygen concentration through the range studied experimentally (i.e., up to 24 cm³/liter); at *p*H 7.0 it increased with oxygen up to about 18 cm³/liter and then decreased; at *p*H 8.0 it increased up to 14 cm³/liter and then decreased. The greater the concentration of OH^-, the smaller becomes the concentration of oxygen needed to hinder the reaction.

The inhibitor need not necessarily be a salt with an anion giving a sparingly soluble salt with the metal. Potassium chromate solution added to ferrous sulfate solution produces a precipitate containing (in general) iron and chromium; it appears unlikely that an iron cation could evade "arrest" while entering a liquid containing chromate ions (if no other anions are present, except of course OH^-). The fact that iron keeps bright in a chromate solution indefinitely needs no special explanation. Again, where a substance is itself an oxidizing agent, either more powerful or more soluble than oxygen itself, it is likely to act as an inhibitor in the same way as oxygen, but more effectively; nitrites may be a suitable example, but here again they may act by oxidizing a ferrous compound to the less soluble ferric compound.

The mechanism sketched above suggests that at a weak spot a metallic cation may be arrested either by atomic oxygen or by OH^-. In the first case, an electron must pass outward through the film at the same weak spot. In the second case, the electron is already provided, but it is necessary (if no charge is to accumulate) for adsorbed atomic oxygen to be converted to hydroxyl ions at points on the surrounding region; since, with a liquid of good conductivity, the region where this may happen is large compared with the area of the weak spot, an oxygen concentration too low to insure direct arrest of emergent cations at the weakest points may suffice if OH^- is present in sufficient concentration—explaining Groesbeck and Waldron's results. It should be added that an "arrest" of emergent cations by OH^- may well lead to anhydrous metallic oxide, by loss of water.

Where a compound inhibits merely by adsorption of its molecules unchanged at weak spots on the surface, no oxygen is needed for the formation of the obstructive layer, and no hydrogen for its removal. If a restrainer of corrosion contains ionizable hydrogen, it can be written HX. If it is adsorbed "unchanged" both H^+ and X^- cling to the metallic surface—not necessarily at the same points—and no reducing action is needed to remove HX molecules; thus the protection is likely to be imperfect and fleeting. If however the salt MX_n is sparingly soluble (where n is the valency of the basis metal M), we can under oxidizing conditions obtain a layer of MX_n, which can only be removed by reducing conditions. Here there is better chance of reliable protection, which may last to some extent even when the liquid ceases to contain HX. There is, however, no evidence that a single molecular layer of MX_n gives appreciable protection. In all cases where films have been stripped from metal after immersion in an inhibitive solution, they are found to be many molecules thick; if a single molecular layer had been protective, it would have prevented further thickening.

Electron Diffraction Examination of Films

The argument developed suggests that both oxide and a compound representative of the inhibitor will be found in the films taken from passive metal. The authors (31) once estimated chemically the constituents of the film stripped (by the aqueous iodine method) from iron previously immersed in chromate solution: it was found to be mainly iron oxide with small amounts of chromium compounds, which, however, were still smaller if there had been a period of air exposure between the abrasive preparation of the surface and its immersion in the chromate solution; such an air exposure would heal some of the weak places in the oxide film. Later Mayne and Pryor (32) stripped films (by the alcoholic iodine method) from an iron surface prepared by pickling and subjected to chromate solution *without* intervening air exposure; electron diffraction studies of the film showed it to consist of γ-ferric oxide, the form of oxide that is produced by air exposure at ordinary temperature. No chromium compounds were detected, but it is possible that they would have escaped detection by the methods then available. Later, a more sensitive electron-diffraction method was developed, and used by Mayne and Menter to study films stripped from iron after immersion in other inhibitive solutions. In every case, γ-ferric oxide was found, but the film taken from iron immersed in disodium hydrogen phosphate solution also contained considerable quantities of hydrated ferric phosphate (33); that taken from iron immersed in sodium hydroxide contained small amounts of FeO(OH) as well as Fe_2O_3 (34). On the whole, the facts fit the picture of the mechanism presented above.

Mixtures of Inhibitive and Corrosive Chemicals

In all cases where an inhibitor serves to arrest escaping cations at a weak place in the film, it is destroyed in so doing. If an inhibitor of the class discussed above is present along with an excess of a corrosive salt (one containing an anion that forms a soluble salt with the immersed metal), it is likely that the inhibitor soon becomes exhausted around the weak points. At such points the metal starts to

pass into solution as a soluble salt, and is precipitated when it reaches a place where inhibitor still remains; in general, a membranous precipitate will be formed at the surface that separates the exhausted from the unexhausted regions. Thus, if iron is placed in water containing sodium phosphate and chloride in proportions such that corrosion is prevented over the greater part of the surface but not at the weak points, the latter become covered with membranous blisters that must hinder still further the access of inhibitor and oxygen to the points where they are needed if corrosion is to be arrested. The combination of large cathode and small anode produces intensified attack on the parts below the blisters.

If the substance thrown down by interaction between the metallic cations and the inhibitor anions is one that does not readily form a membrane, such intensification can be avoided. Thus, while a chloride-chromate solution acting on iron may produce perforation more rapidly than a chloride solution free from chromate, a chloride-chromate solution acting on lead does not produce intensified attack, even though the chromate is present in amounts insufficient to stop corrosion altogether—as shown in the early work of Roetheli and Cox (35). Palmer (36) found that, in chloride-phosphate solutions acting upon iron, the ferrous phosphate formed at points of localized corrosion tends to assume a membranous form, whereas if chromate as well as phosphate is present (but in proportions too low to arrest corrosion entirely), the (ferric) product thrown down is loose and nonmembranous. Thus attack, although not prevented, is at least not rendered more intense. Palmer's phosphate-chromate mixtures may, for some purposes, provide an inhibitive treatment which is efficient (in the sense that it prevents corrosion if added in appropriate quantity) and safe (in the sense that it does not intensify attack even where it is unable to stop corrosion altogether). Similar mixtures have been developed independently by Kahler and George (37) and are stated to be alalready in industrial use.

Pitting in Absence of Added Inhibitor

Since every aqueous salt solution contains hydroxyl ions, the question often arises as to whether the anodic product formed at a weak place in a film is a soluble salt or an insoluble hydroxide. It has, however, been pointed out elsewhere (38) that where the *p*H of the solution is so low that the hydroxide would (if formed) be unstable, it is not formed at all under conditions close to equilibrium, and the corrosion product is a soluble salt of the metal. However, where the *p*H is sufficiently high that a salt solution, if formed, would hydrolyze (to hydroxide or basic salt), then the product to be expected under conditions close to those of equilibrium is the hydroxide or basic salt; thus, the film thickens instead of breaking down.

It might be expected from these arguments that iron or zinc, placed in, say, a neutral chloride solution, would develop hydroxide, and observations on iron or zinc immersed for short periods in such solutions suggest that this is indeed the case (39). Zinc, for instance, placed on $N/10$ potassium chloride, gives only adherent matter for the first 40 minutes, an observation which was originally interpreted differently. However, any discharge of OH^- renders the liquid acid, and a state is soon reached at which the anodic product is Fe^{++} or Zn^{++}, the metallic hydroxide being now precipitated at a distance from the metal, where the anodic product meets the OH^- produced at the cathode.

With metals which form especially easily-hydrolyzed salts, the situation is different. Aluminum, partially immersed in potassium chloride, under the same conditions as those maintained in the experiments on iron or zinc, may develop practically no soluble salt for an appreciable period; the anodic reaction at surface blemishes (which furnish weak spots in the surface film) leads to white spots of adherent hydroxide. Only after a day or so do aluminum ions begin to pass into the solution; this probably occurs when sufficient acidity has appeared to render possible the formation of soluble aluminum chloride. The latter interacts with the potassium hydroxide well away from the metal, so that the liquid gradually becomes cloudy.

A similar state of affairs exists in the case of tin immersed in chloride solutions (40). No visible attack occurs for hours or days, and during this period, which is longer for the more dilute chloride solutions, the electrode potential rises, indicating an initial film repair, owing to the anodic production of very sparingly soluble tin hydroxides; but localized breakdown ultimately occurs because of the concomitant production of acidity at the anodic points, which ultimately allows soluble tin salts to form. The theory of film breakdown based on the local formation of acidity has been further developed for the case of iron (41); a much smaller lowering of *p*H is here required for the formation of soluble products, and consequently attack begins more quickly and spreads out more readily than in the cases of aluminum and tin.

Films Containing Sulfur

A "pure" sulfide usually contains more lattice defects than a pure oxide. This is illustrated by the assignment of the formula $Fe_{11}S_{12}$ to pyrrhotite (it is really ferrous sulfide, FeS, with about one-twelfth of the places on the cation lattice vacant and about

one-sixth of the ferrous ions replaced by ferric ions, so as to keep the whole electrically neutral). The presence of a small amount of sulfur in an oxide lattice will certainly introduce lattice defects—perhaps more than might be expected merely on the grounds that it is a "foreign atom." The fact that oxidation of iron at high temperatures in air containing sulfur compounds is greater than that in pure air is probably partly due to this cause. Copper, which remains bright in pure air at room temperature, suffers discoloration if traces of hydrogen sulfide are present, developing at room temperature the same sequence of interference tints as appears in pure air at slightly higher temperatures. If exposed to air containing sulfur dioxide, it becomes brown, and the film is apparently a sulfide/oxide solid solution. Vernon (42) has shown that after an initial period of linear growth the film develops according to the parabolic law, and the value of k in the equation $dy/dt = k/y$ is proportional to the active sulfur content of the atmosphere, possibly because it is proportional to the number of defects introduced into the film.

Homer (43) has shown that a polished steel surface, wetted with a liquid producing effects near the borderline of corrosion and passivity, starts to corrode at particles of rolled-in scale or sulfide inclusions; silica and alumina do not act as starting-points, and indeed only a fraction of the sulfide particles act in that way. It is likely that a film which is protective elsewhere may contain defects, and thus allow the outward passage of cations in the neighborhood of sulfide inclusions. If a scratch-line is present in the surface, however, the corrosion starts upon it in preference to the inclusions, while if the whole surface is roughened, the effect of inclusions ceases to be apparent. Similarly, Mears (44) has shown that, under borderline conditions, the probability of corrosion is increased by sulfur in the steel, or by loose sulfide particles placed on the surface.

Alternate Healing and Breakdown

A method has been developed (45) for recording the position of corroding spots on iron placed in a liquid of borderline properties, by absorbing the iron salts in filter paper and then converting them into prussian blue by the action of potassium ferrocyanide; the pattern of blue spots shows the places where corrosion is proceeding. If the specimen is kept in liquid containing no large amounts of oxygen, the pattern remains unchanged, showing that the corrosion continues where it has already started but does not set in at fresh places. If, however, free exposure to oxygen occurs, most of the points of corrosion disappear, and subsequently points of corrosion develop at new places. This probably means that, either through thermal movement or by cracking under internal stress, the film is continually developing new weak places that are potential sites of corrosion. If there are already many sites of corrosion operating, no corrosion starts at the new points, since the excess of electrons left by the passage of cations at the already corroding points gives a species of cathodic protection to the rest of the surface. When most of the old points have healed as a result of air exposure, the cathodic protection is no longer effective and corrosion at new places can set in. The disappearance of the old points of corrosion and the appearance of new ones was referred to as "crack-heal" when the observation was first made, but the name may be misleading since the appearance of new places of attack may be due to thermal movement of atoms rather than to cracking under mechanical stress. However, the experiments show why it is necessary to have a supply of inhibitor constantly present in a water, if corrosion is to be prevented; although the concentration needed diminishes when the major weak points connected with surface defects have been dealt with. The possibility of decreasing the inhibitor concentration as time goes on was noted by Darrin (46) in the case of chromates; a similar decrease is possible with some other inhibitors.

Summary

1. The fact that certain alloying elements that confer resistance to high temperature scaling of metals also confer resistance to wet corrosion at low temperatures suggests that the outward movement of cations through an oxide film, the usual factor controlling high-temperature scaling, is also important in the onset of wet corrosion.

2. Iron or zinc, whirled in water containing dissolved oxygen, so as to replenish oxygen constantly at all parts of the surface, remain unattacked. If whirling stops, attack sets in, presumably at spots where the oxygen supply is insufficient to "arrest" the emerging cations. Where the film is one through which outward ionic movement will certainly be slow, as on stainless steel, a scanty supply of oxygen suffices to prevent attack.

3. If the oxygen is insufficient at some place where the film contains faults favoring a rapid emergence of cations, the cations pass into the liquid, becoming hydrated; electrical neutrality is preserved by the cathodic reduction of oxygen at the surrounding area where the film is less faulty.

4. Inhibitors serve to arrest cations that would otherwise emerge. Some are oxidizing agents, and provide in effect a highly concentrated source of oxygen. Others are effective only if molecular oxygen is also present.

5. Sulfides favor both high-temperature oxidation and also the onset of corrosion, probably by increasing the number of lattice defects in the oxide film and thus facilitating the outward movement of cations.

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